STUDIES ON
THE THERMODYNAMICS OF ION ASSOCIATION
IN AQUEOUS SOLUTIONS

A Thesis

Submitted to the University of Glasgow

for the degree of

DOCTOR OF PHILOSOPHY

BY

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August, 1965.

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FOREWORD.

The work described in this thesis was carried out in the Physical Chemistry Department of the University of Glasgow, which is under the direction of Professor J. Monteath Robertson, F.R.S.

I wish to express my sincere thanks for the guidance and encouragement given by Dr. G.H. Nancollas under whose supervision this work was performed. Thanks are due to Dr. H.S. Dunsmore who wrote all the computer programmes, and to the staff of the engineering workshop for the construction of the calorimeters.

I am indebted to the Science and Research Council for the award of a Maintenance Grant, from October 1962 to October 1965, which made this research possible.

A sensitive calorimeter has been used to measure the heats of formation of complexes in dilute aqueous solution. With a knowledge of the accompanying free energy changes, the corresponding entropies of association have been calculated. Knowledge of entropy and enthalpy changes provide a clearer insight into the nature of the chemical reaction than does the free energy change alone.

The thesis is divided into five parts. Part I describes the development of the calorimeter and its use in measuring the heats of formation of complexes of divalent ions of the first transition series with succinate and malonate anions. The work was done at low ionic strength so that activity coefficients of the ionic species could be estimated from the Debye - Huckel equation. Since an accurate ΔH is dependent on a reliable value of the association constant it was necessary to determine the association constants for zinc succinate complexes and this is described in Part II. The association between zinc and succinate ions was investigated using the following cell.

H_2, Pt / H_2Succ, NaOH, $ZnCl_2$ / AgCl, Ag.

Since the dissociation constants of succiric acid are not widely separated the data was processed on an English Electric KDF9 computer for all species present in solution assuming two complexes, zinc succinate and zinc hydrogen succinate, were present. The thermodynamic properties of complexes with the dicarboxylate anions are discussed in Part III.

A calorimetric investigation of the heats of formation of mono-thiocyanate complexes is described in Part IV. The thiocyanate ion has the ability to bond through either the sulphur or the nitrogen atom and it was hoped that information concerning the nature of the donor atom could be obtained from a knowledge of the thermodynamic properties of the complex. A brief IR study of the CN stretch frequency (2,100 cm^{-1}) was undertaken to provide additional information on the bonding.

Part V consists of a potentiometric investigation of the third and fourth dissociation constants of Di-(2-aminoethoxy) -ethanetetraacetic acid (E.G.T.A.) using a glass electrode system. This work was carried out at constant ionic strength of 0.1M to complement additional research being made in this field.

GENERAL INTRODUCTION

The division of electrolytes into two principle types, strong and weak, was proposed early this century. The former were considered to be dissociated at all concentrations while the latter tended to complete dissociation only in very dilute solutions. Conductivity measurements showed that weak electrolytes obeyed the law of Mass Action whereas strong electrolytes did not. There was much speculation on the reason for this anomaly before the classical work of Debye and Hückel [1] provided an explanation which would not require any undissociated strong electrolyte molecules. The Debye - Hückel theory calculates the electrical potential ψ at a point in the solution in terms of the concentration and charges of the ionic species and the physical properties of the solvent. This is accomplished using a statistical mechanical distribution formula combined with the Poisson equation for electrostatics.

The Debye - Hückel theory is based upon a qualitative description of an ion in solution being surrounded by ions of opposite charge, when these ions are close together then the same approximations used in the derivation of the theory are no longer valid. For example their mutual electrostatic attraction can be greater than the opposing thermal effects which tend to keep a random distribution of ions in solution. This led Bjerrum [2] to propose the existance of a new species in solution which he called associated ion pairs. Considering only electrostatic forces he calculated the probability H of an ion of the 'i'-th type being present in a volume element between 'r' and 'r + dr', from a chosen ion of the 'k'-th type.

$$H = \frac{NCi}{10^3} \; 4\pi r^2 dr e^{\Phi/kT}$$

In which c_i is the molality of species 'i', and $4\pi r^2 dr$ is the volume element with radii 'r' and 'r + dr'. Φ is the work necessary to separate two ions and $e^{\Phi/kT}$ is a Boltzman factor expressing the extent to which the electrical forces in solution favour the configuration. If the solvent is considered as a homogenous medium with a dielectric constant D, then from Coulomb's law,

$$\Phi = -z_i z_k e^2 / Dr.$$

For the case in which ions are of opposite sign, then as r increases there is decreasing probability of finding any 'i' ions in a unit of volume but since the volume of the shell increases the two opposing effects combine to give a minimum at a distance 'q' such that; for distances less than 'q' H increases rapidly and for distances greater than 'q' H increases slowly, where

$$q = z_i z_k e^2 / 2DkT.$$

The work required to separate these ions at this distance is 2kT, thus the energy necessary to separate the ion pair is four times as great as the average kinetic energy per degree of freedom (Bjerrum then showed that q = 3.5 Å at T = 18° C). For 1:1 electrolytes, ions which are large will associate to a very small degree but those with $r_i + r_k < 3.5$ Å will have considerable association. When this occurs equilibrium constants for these associations can be written in exactly the same manner as for normal molecular dissociation reactions.

Considering only electrostatic forces and assuming ions to be point charges, Bjerrum's theory does indicate that ion association is most probable in cases where valency is high and dielectric constant low. These predictions are borne out by experimental results [3,4]. In dilute solutions, at distances greater than Bjerrum's 'q', the physical properties of the ions can be adequately dealt with by the Debye - Hückel theory from which it is possible to derive a theoretical value for the activity coefficient. This is necessary if a thermodynamic interpretation of the solutions properties is to be attempted.

The mean activity coefficient of an electrolyte can be expressed by, the equation,

$$\log f_{\pm} = \frac{-A z_1 z_2 I^{\frac{1}{2}}}{1 + B\mathring{a}I^{\frac{1}{2}}} \qquad \ldots\ldots\ldots(1).$$

Where the constants A and B involve the absolute temperature and dielectric constant of the solvent:

$$A = \frac{1.8246 \times 10^6}{(DT)^{3/2}}, \quad B = \frac{5.029 \times 10^9}{(DT)^{\frac{1}{2}}}$$

The derivation of this equation is such that $-Az_1z_2 I^{\frac{1}{2}}$ gives the effect of the long range coulombic forces, while $1 + B\mathring{a}I^{\frac{1}{2}}$ shows how these are modified by the short range interactions between the ions. The parameter $\mathring{a}$ is defined as the distance of closest approach of the free ions or the mean ionic diameter of the ions. In the derivation of the Debye - Hückel potential for an ion no account was taken of short range

interactions between ions and solvent molecules. Hückel[5] attributed deviations at high ionic strength to changes in the dielectric constant. Since these are likely to be linearly related to the concentration they can be included in the expression for $\log f_{\pm}$ by introducing an empirical factor bI,

$$\log f_{\pm} = \frac{-Az_1z_2I^{\frac{1}{2}}}{1+B\mathring{a}I^{\frac{1}{2}}} + bI \quad .....(2).$$

When suitable values of parameters $\mathring{a}$ and b are chosen this equation can represent the activity coefficient up to quite high concentrations. All the expressions discussed deal with symmetrical electrolytes. In mixed electrolyte solutions a mean activity coefficient can be found for any ion valency but it becomes difficult to attach any physical reality to $\mathring{a}$, the distance of closest approach of the ions. In mixed electrolyte $\mathring{a}$ is really a parameter correcting for a variety of theoretical imperfections. The value of the dielectric constant of the solvent used in the Debye - Huckel equation is subject to speculation since its value in the immediate vicinity if an ion will be different from that in the bulk. The extended form of the Debye - Hückel equation proposed by Davies [6] has been used in this work,

$$\log f_{\pm} = -A\, z_1z_2 \left[\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - 0.2I\right] \quad .....(3).$$

The mean activity coefficient calculated from this equation has been shown to give good agreement with the experimental value for 1:1, 1:2, 2:1, electrolytes up to 0.1M.

The classical theories were built upon electrostatic considerations involving only coulombic forces between the ions but it is also possible that covalent forces will be involved in the formation of complexes and ion pairs. These will be of a short range nature in comparison with the electrostatic forces. The presence of charged molecular ions such as $(Hg_2)^{2+}$ in aqueous solution is due to the reduction of the electrostatic repulsion by the polar nature of the solvent.[7] Charged ion pairs such as $(PbCl)^{+}$ have been suggested as a contributing factor to the low conductivity of aqueous solutions of lead (11) chloride. In this case, in addition to the electrostatic forces, there are short range quantum mechanical forces of attraction. The effect of the high dielectric of water will be to reduce the electrostatic contribution.

In order to differentiate between these two forms of association it has been proposed that the Bjerrum - type are called ion - pairs and the covalently dominated species, complexes. An other suggestion was that the word ion-pair be used to describe species having one or more water molecules interposed between the ions and that the term complex should be kept for an association which excluded interstitial solvent molecules. An approximate method of assigning associated species to one type or an other can be made using the Bjerrum treatment. If the association constant for the reaction is known, integration in the equation,

$$K = 4\pi \int_a^q \exp.(z_+z_-e^2/DkTr)\, r^2 dr ,$$

will give a value of the distance of closest approach. If this is very small in comparison with the theoretical 'q', then it is taken as evidence of covalency. This method of obtaining information on the nature of the bonding should be used with caution since Bjerrum's 'q' value is too large because the potential from the surrounding ions was neglected in deriving the expression for 'q'.

The formation of a metal complex is often accompanied by a change in the light absorption of the complex relative to that of the free metal ion or ligand. A change in the visible spectrum is frequently attributed to the formation of inner-sphere complexes whereas changes in the charge transfer U.V. region are associated with outer-sphere or ion-pair formation.

Nuclear Magnetic Spectroscopy has become increasingly widely used in studying complexing in solution. The chemical shifts for solutions containing $Tl^{205}(III)$ in the presence of varying concentrations of halide ions have been interpreted in terms of the formation of a variety of thallic halide complexes.[8]

Covalent interaction in solution will give rise to new Raman lines characteristic of the complex formed; moreover the integrated intensities of the lines, for a given species, appear to be proportional to its concentration. A study of Raman spectra, therefore, will afford more direct evidence of specific interaction in electrolyte solutions than can be obtained by the more classical methods. It has been suggested that pure ionic association will be accompanied by a Raman effect which could be at least a hundred times less dense

and therefore escape observation.[9]

In this study the associated species will be referred to as complexes and the association is considered to have contributions of both electrostatic and covalent natures.

PART I

Calorimetric Heats of Formation of Transition Metal Dicarboxylate Complexes.

Calorimeters used in Enthalpy Estimations.

With the revival of interest in complex equilibria in solution a considerable number of association constants have been determined.[10] In many systems the formulae and the evidence for the existance of ion pairs and complexes can be established with some certainty. In order to obtain a better understanding of such reactions it is desirable to regard the free energy change as resulting from changes in enthalpy and entropy components.[11] Many attempts have been made to calculate ΔH from the variation in equilibrium constants with temperature but the accuracy obtained by this method can be very poor.[12] Data for the same system has been known to be in disagreement by as much as the sign of the entropy or enthalpy change.[13] It is much more reliable to obtain ΔH values by a direct calorimetric method. Calorimetric measurements, even of moderate accuracy, will produce results of a higher quality than those obtained by the temperature coefficient method.

A number of calorimeters have been developed for the measurement of heats of solution and heats of complex formation. Most of them are of the constant environment type, the temperature of which is controlled such that a measured thermodynamic property can be assigned to this temperature. Most of these calorimeters have a number of common features,

(a) a heating element of known resistance through which a known current can be passed for a known time.

(b) a temperature sensing element.

(c) a device which will keep the two

reactants separated until mixing.

(d) a stirrer to ensure homogeneity.

A calorimeter, whose design has become the standard for many others, was developed by Pitzer.[14] This was designed to allow sensitive measurements at low concentrations of reactants in order to minimise uncertainties due to interionic effects. Pitzer's calorimeter was designed with a copper resistance thermometer (~100Ω) incorporated as one arm of a D.C. Wheatstone bridge. The calorimeter was kept at constant temperature in a water bath. The internal heating element consisted of insulated copper wire protected by a thin silver sheath. An electronic timer was used to record the duration of the heating currents to 1/200 of a second. Mixing was effected by breaking a glass phial on the blade of the rotary stirrer. Temperature changes of 3×10^{-4} °C could be detected. A calorimeter of similar design has been used in recent work by Staveley.[15] The only significant development being the mixing device, which was a glass bottle with ground glass joints top and bottom. Both stoppers were attached to the same glass rod and were released by lifting this rod. A temperature sensitivity of 5×10^{-5} °C was reported for this calorimeter.

More recently automatic recording of temperature changes have been introduced. In calorimeters reported by Cobble[16] and Izatt[17] the output from a D.C. Wheatstone Bridge was amplified and fed to a chart recorder. Thermistors have been developed which are very stable and have a large temperature coefficient of resistance and these

have been incorporated into a number of calorimeters.[17,18]

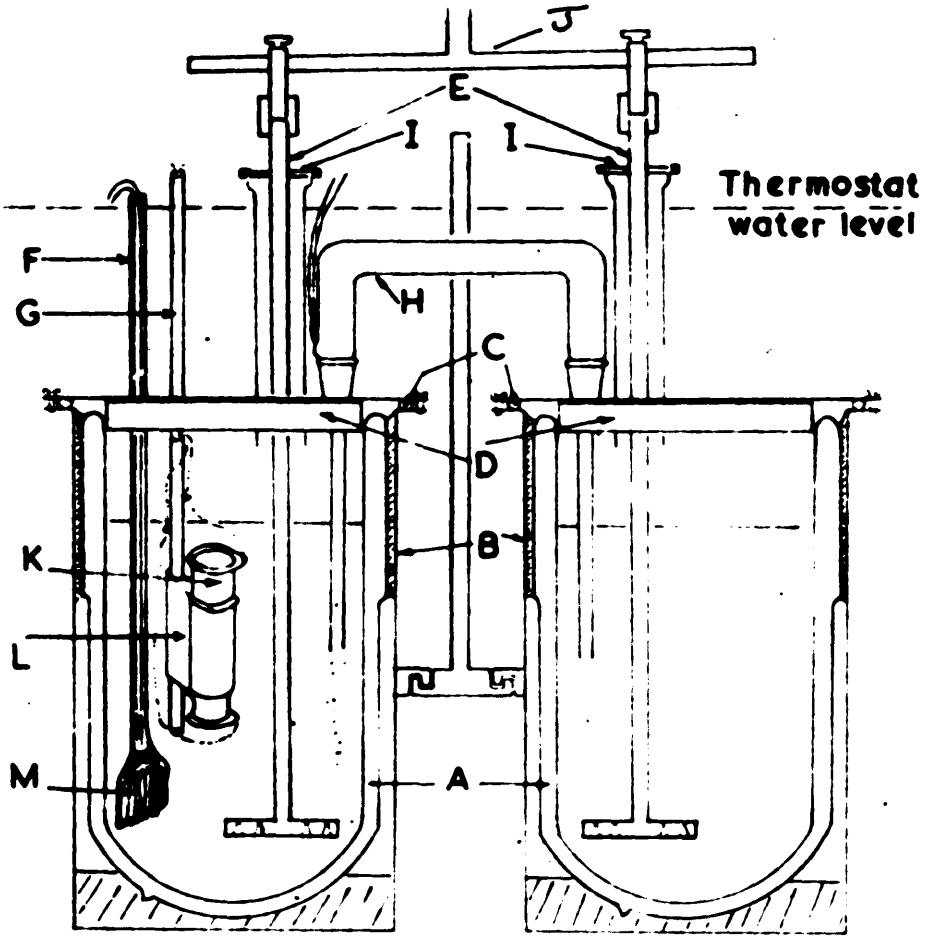
In order to study stepwise formation of complexes and polynuclear species in solution, titration calorimeters have been developed by Scandinavian schools.[19,20,21,22,23] These calorimeters differ from those previously described, in that graduated additions of one reactant must be made. Leden and Sumner[20] used a pipette which could be opened into solution by releasing a ground glass stopper. This could then be closed and recharged, without withdrawing the calorimeter from its thermostat. A disadvantage was the limitation of the addition due to the size of the pipette. In order to overcome this difficulty Danielson[21] proposed that additives of titrant could be made through a fine capillary which was fed from a thermostated spiral burette. Since successive reactions could increase the temperature of the calorimeter contents an air cooling device was introduced to bring the solution temperature back to that of its environment between successive exothermic reactions.

APPARATUS.

Thermopile Differential Calorimeter:- (Fig 1).

In the present work differential calorimeters have been developed for the measurement of heats of formation of complexes. The instrument was modelled on the design of Lange,[24] who considered that since heats of dilution of the salts he was measuring were very small, the heat effects produced experimentally must be sharply defined and all secondary effects (heat of absorption and conduction) be reduced to a minimum. To this effect he designed a calorimeter which was divided into two halves whereby any thermal disturbances from outside were duplicated in both vessels. The twin compartments were fashioned from a large Dewar flask by placing a partition down the centre. A sensitive temperature sensing element was supported on the central position with an equal number of junctions on either side.[25,26] The sensitivity of Lange's calorimeter was such that temperature changes of 2×10^{-7} °C could be detected. The major features of this instrument were incorporated in the differential calorimeter built, a diagram of which is shown in Fig. (1).

The Dewar flasks(A Fig 1) used were silvered vessels of 1,500 cc capacity and were set in brass containers (B Fig 1) whose internal diameter was approximately 1cm greater than the external diameter of the Dewar. The base of the Dewar was supported on a cork ring and steel wool packed the space between the container and the glass surface. A layer of Araldite adhesive round the top surface of the steel wool sealed the Dewar into the container.



The calorimeter with fittings.

Fig. 1

Each half of the calorimeter was fitted with a brass lid which seated on to a rubber O-ring (C Fig 1). The lid was effectively sealed by tightening six wing nuts round its circumference. In order to minimise the air space above the solution each lid had a Teflon disc (D Fig 1) approximately 8cm thick cemented to its underside. Holes were bored in the lids to accommodate the stirring rods (E Fig 1), the supports for the heating element (F Fig 1)and the mixing device (G Fig 1), and B24 sockets for the thermopile (H Fig 1).

All glass to brass fittings were made watertight with Araldite cement. The thermopile consisted of sixty eureka (20 S.W.G. Vactite Wire Co. Ltd. Bootle, Lancs.)-copper (34 S.W.G. London Electric Co. and Smiths Ltd.) junctions made by soft soldering the two wires together. These were arranged such that they lay evenly throughout the entire depth of the solution. The thermopile was placed inside a length of large diameter rubber tubing on to which B24 cones were cemented at either end. The heating element (M Fig.1) was made from nichrome wire (32 S.W.G.) wound round a glass former and the ends spot welded to platinum wire loops which were sealed into the heater support tube (F Fig.1). Connection was made through two pairs of copper wires soldered to the platinum loops. The surface of the heating element was insulated by repeated coatings of Formvar in ethylendichloride solution. The solution container (K Fig.1) inside the calorimeter consisted of a glass tube of 17mm. diameter, having a total capacity of 12ml. The ends of this tube were sealed with rubber bungs cemented on to Perspex

supports. Solutions were mixed by pulling nylon threads attached to these supports. The nylon threads passed out through the glass support tube (G Fig.1). Each Dewar was stirred by a vibrating glass disc at the end of a glass rod (E Fig.1) which passed through a rubber diaphragm (I Fig.1) before being joined to a common horizontal bar (J Fig. 1) by an adjustable chuck. The bar was activated by a central vibratory motor (Vibro-Mischer, Messrs. Shandon and Co. Ltd. England). The advantage of the vibro-stirrer is that it eliminates heat conducted from bearings which are necessary in a rotary stirrer. Vertical movement in the stirring disc was approximately 1-2mm.

The calorimeter was placed in a large water filled thermostat and the temperature controlled by means of a large capacity mercury-toluene regulator in conjunction with a Sunvic proportionating head. The heating element was a 250 watt bulb. A cooling coil was included in the system, through which a slow flow of cold water was maintained.

A diagram of the heating circuit appears in Fig.2. The current was drawn from a 12volt car battery and could be regulated by a wire wound 250 ohm potentiometer (A Fig. 2). The standard 1 ohm resistance (D Fig.2) and the standard Weston cell (E_s Fig.2) were kept in a thermostated oil bath , maintained at 25 C. The current flowing in the circuit was calculated by measuring the voltage drop across the 1 ohm resistance. This was measured on a Cropico potentiometer(Croyden

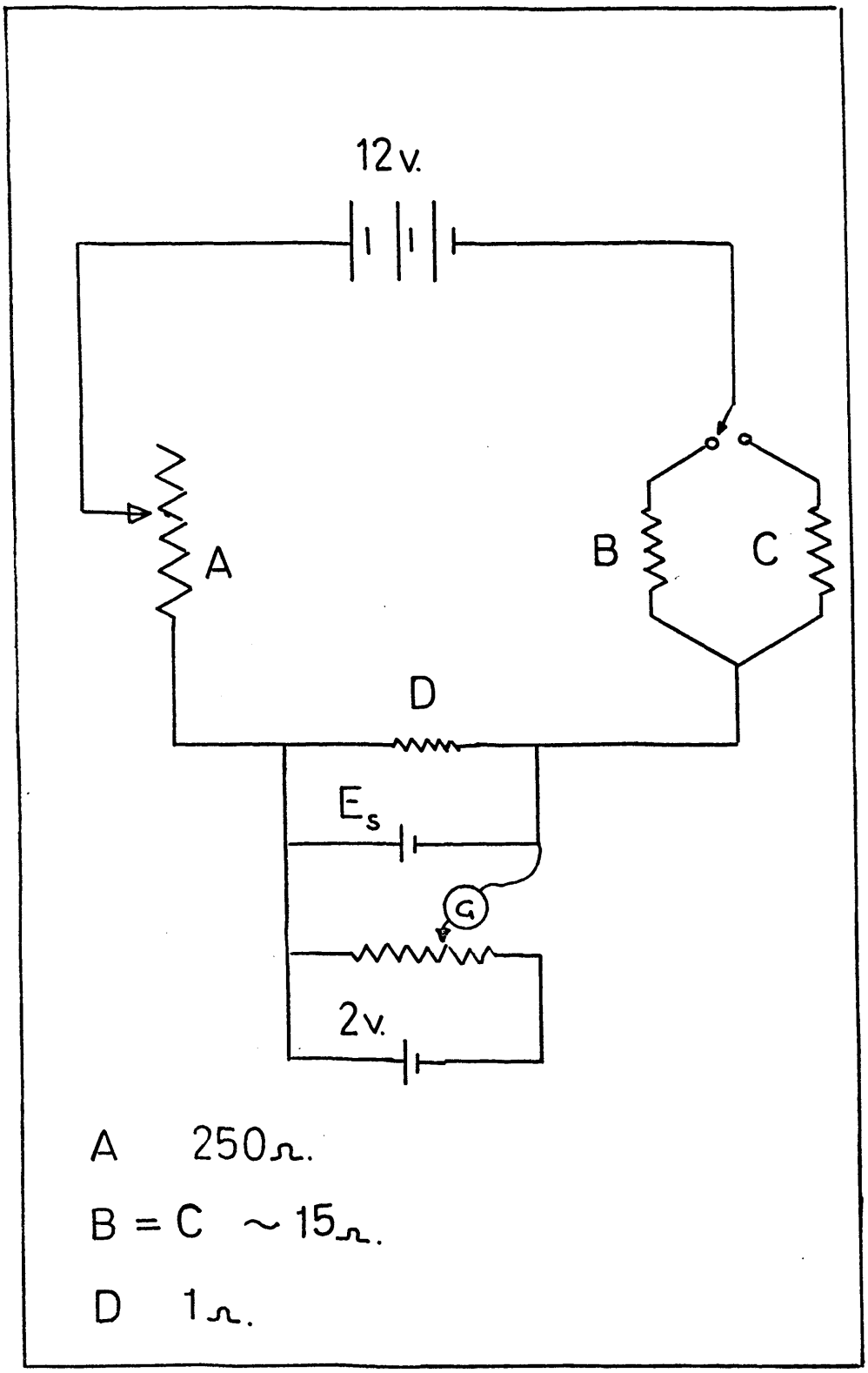


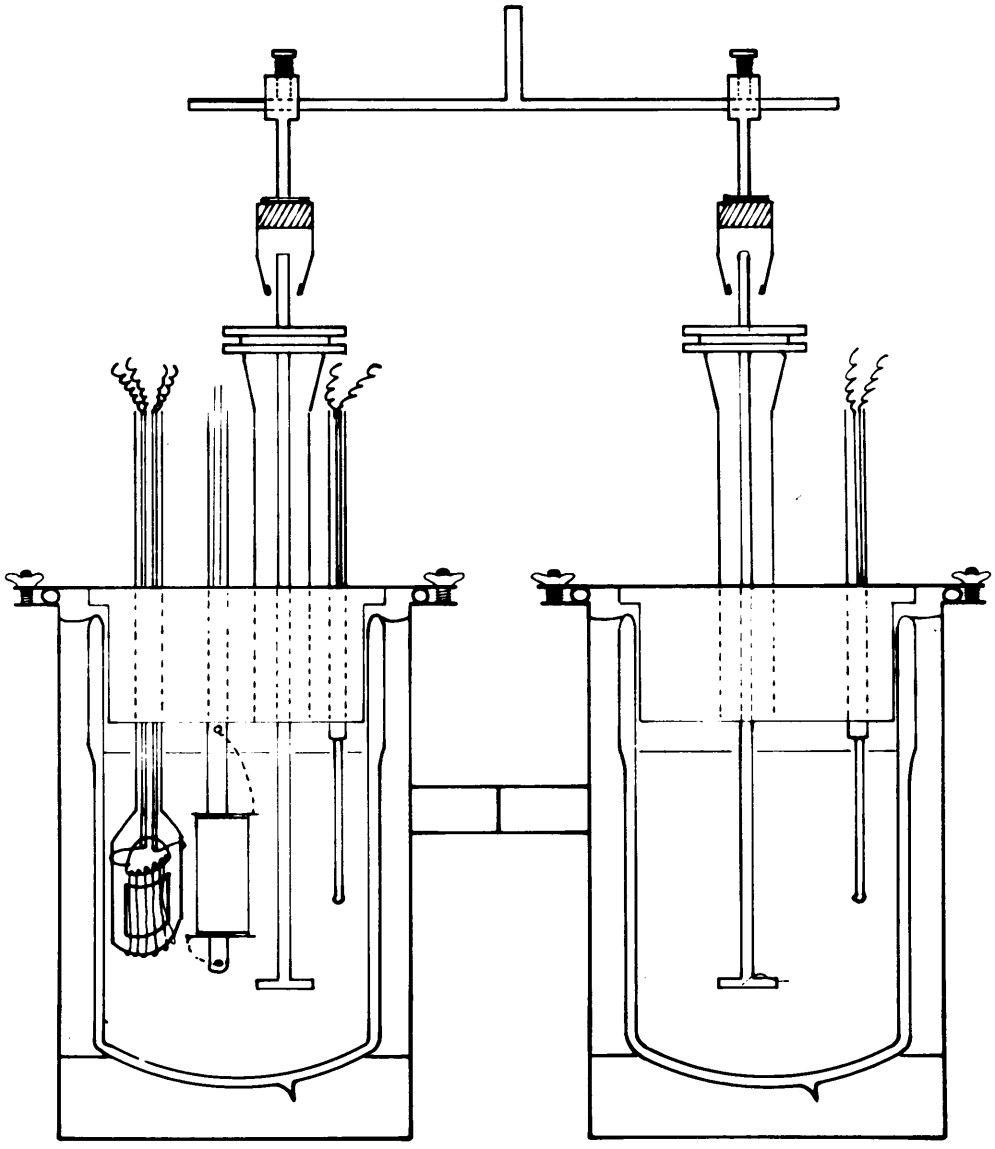
Fig. 2

Precision Instrument Co. Ltd.) to an accuracy of o.lm.volts. Before each run the battery was allowed to stabilise with a 'dummy' resistance (B Fig.2), exactly equal to the heating element (C Fig.2), in circuit. The current could be switched from the dummy to the heating element to supply a known amount of electrical energy to the calorimeter.

The e.m.f.s generated by the thermopile were measured using a Pye Precision Decade Potentiometer (Type 7600), which had an overall range of 2.0V to 0.1microvolts in six ranges. It was standardised by a five dial decade system in the battery circuit and the standard cell voltage was preset with a divider, calibrated from 1.01800 to 1.01900 volts in 10 microvolt steps. A switch incorporated in the circuit enabled spurious thermoelectric e.m.f.s to be detected and eliminated by reversing the switch. A scalamp galvenometer (Pye, type 7904/S) was used as a null detector in conjunction with a Pye galvanometer preamplifier (type 11330). Changes of 0.05 microvolts were easily detected.

Thermistor Differential Calorimeter:- (Fig.3)

For most of the present work a new differential calorimeter was constructed with thermistors as the temperature sensing elements in place of the thermopile. The two thermistors (Standard Telephone and Cable Co., resistance 100k.ohms, Type F15.),



Thermistor Calorimeter

Fig. 3

having a temperature coefficient of resistance of 4% per degree C, were incorporated in the arms of an A.C. Wheatstone bridge and the other two arms, of similar resistance, were made up of high quality Helipot potentiometers. Capacity effects were balanced out by means of two 5-50pF. variable condensers in parallel with the Helipots. The bridge was energised by a stabilised 1 volt A.C. signal of frequency 800c.p.s. The out-of-balance signal was amplified by means of a high-gain amplifier incorporating a phase-conscious synchronous detector (Elesco Electronics, Glasgow) and the output was fed to D.C.amplifier coupled to a 1 m.volt fast response, chart recorder. (Honeywell Controls Ltd., Model Y153x18). A block diagram of the circuit described is shown in Fig.4.

Tests showed that the recorded signal was proportional to the resistance difference between the two thermistors and therefore could be used as a direct measure of the temperature difference between each half of the calorimeter. The noise level was sufficiently low to enable temperature differences of 10^{-5}°C, corresponding to 3×10^{-3}cals. to be detected.

All the internal fittings of the calorimeter, described above, are the same as for the thermopile calorimeter with the necessary reduction in size to fit 300ml.Dewar flasks.(Plate 1.) The usefulness of the calorimeter was enhanced by incorporating a mixing device and a heating element in each side so that each Dewar could be used, in turn, as the blank or reference vessel. The heating circuit was the same as previously described(Fig.2).

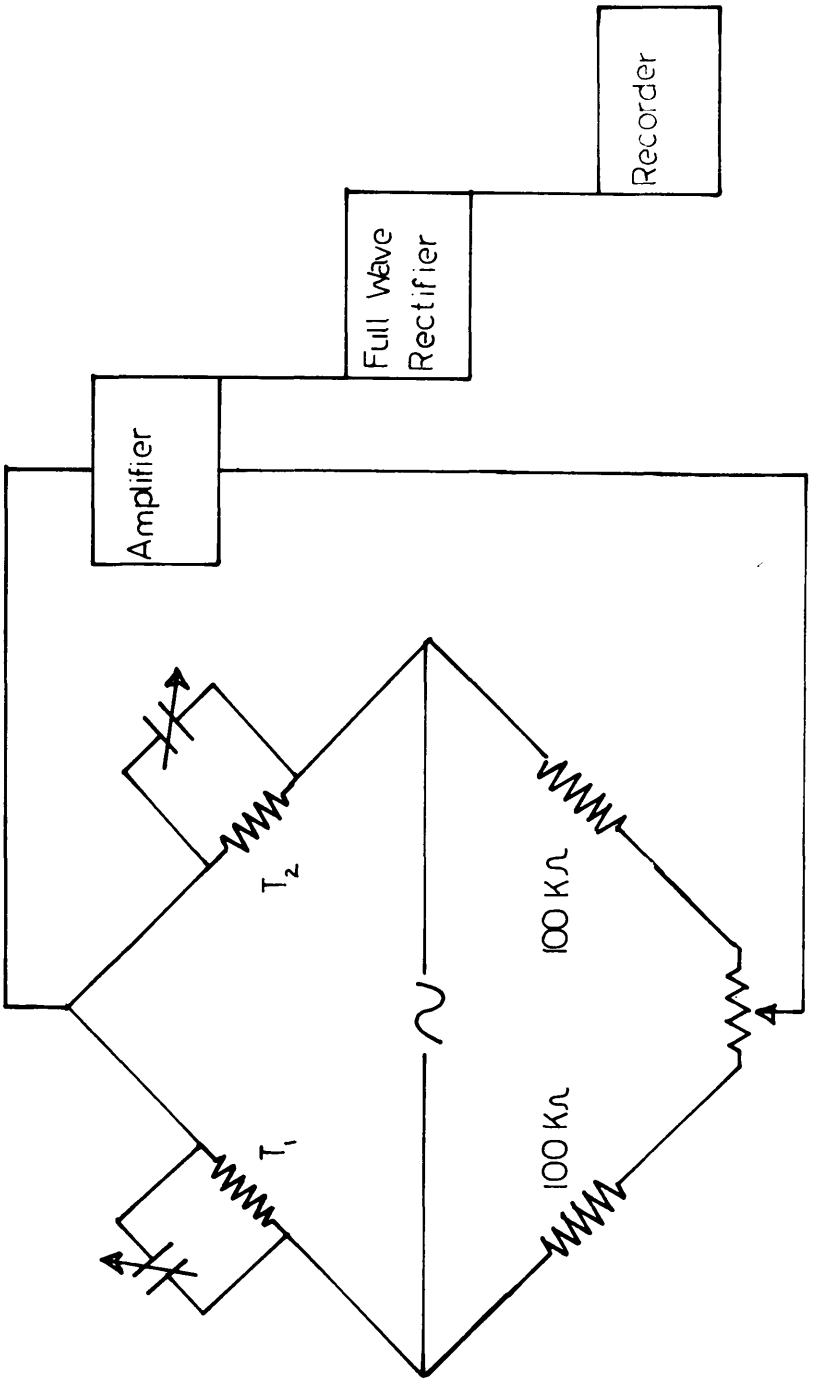


Fig. 4

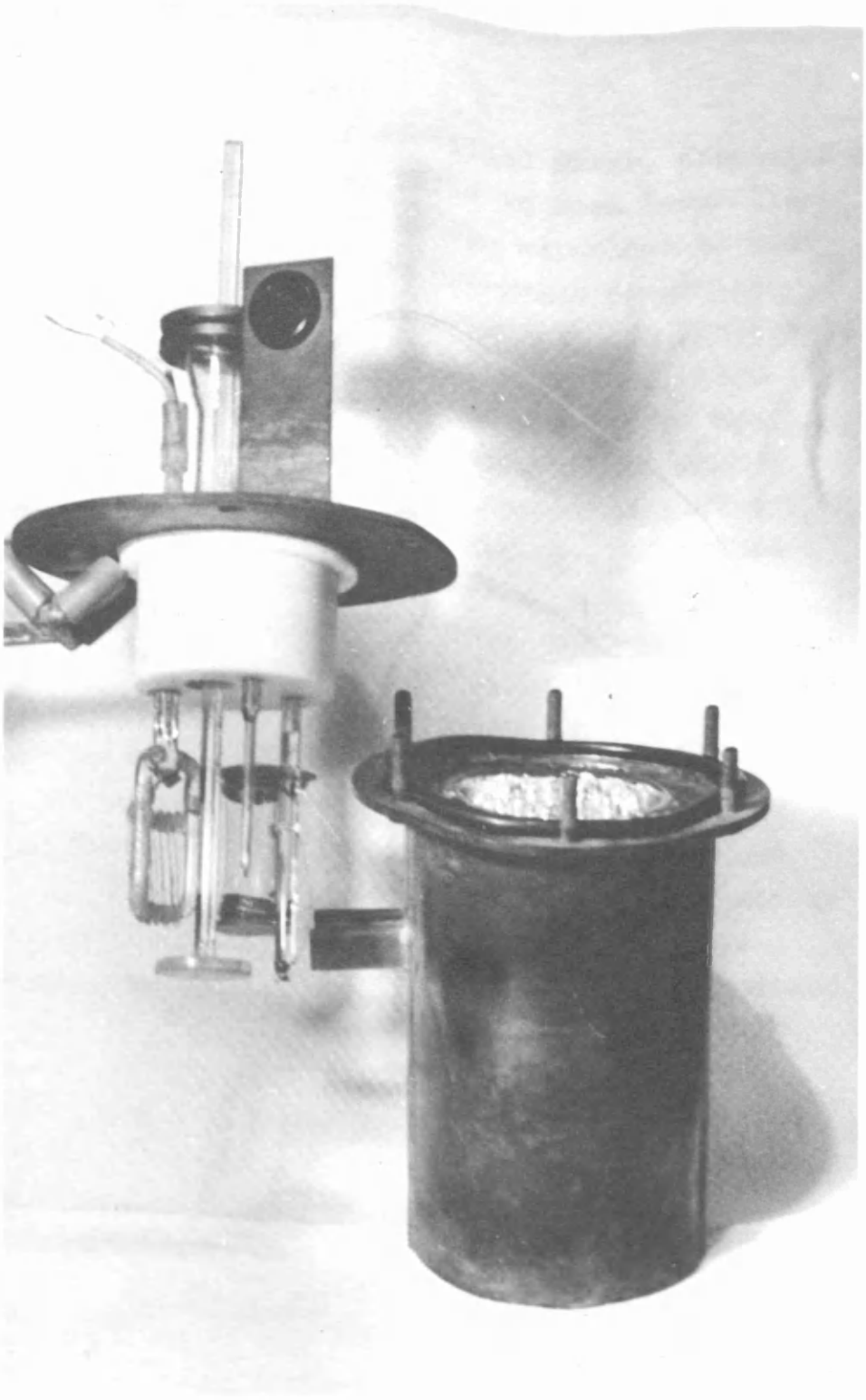


Plate 1

EXPERIMENTAL PROCEDURE.

Thermopile Calorimeter:-

An equal weight of distilled water, approximately 1,000 grams, at 25°C was added to each Dewar flask. The reactants were added to the experimental half of the calorimeter and the apparatus assembled and left in the thermostat overnight to equlibrate. An hour before commencement of a run the vibro-stirrer was started and the battery in the heating circuit allowed to stabilise through the dummy resistance. Readings of e.m.f. were taken every minute and when a steady change was maintained a calculated amount of electrical energy was passed through the internal heating element. The introduction of heat increased the e.m.f./time slope and a typical plot is shown in Fig. 5. A heating period of five minutes, with a current of 0.15 amps, was found to be suitable and this was accurately timed on a stop-clock. After the heating period the e.m.f. settled down to a steady change with time and when sufficient readings had been obtained to establish a constant gradient, the mixing device was opened. The experimental heat change produced a rapid change of e.m.f. which was soon followed by another steady period. A further energy or water equivalent was estimated after the experimental heat change.

The heating curves, Fig. 5, were analysed by Eitel's[27] method. The heat changes were subdivided into three parts, (a) and (r), corresponding to $d\mu v/dt$ in the fore- and after-periods, and (x) to the variation during the change itself. The first temperature reading θ_o(μv.) was at

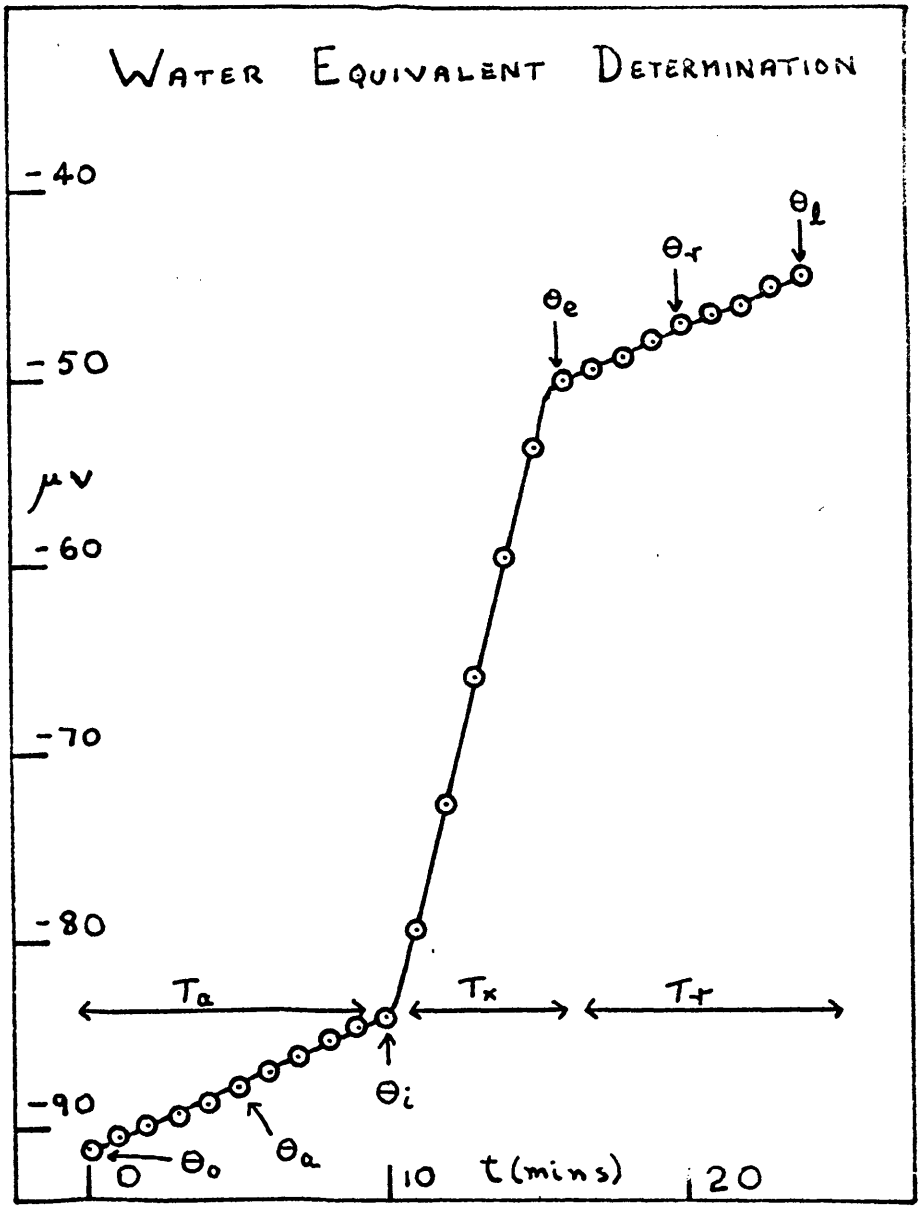

WATER EQUIVALENT DETERMINATION
-40
-50
μv
-60
-70
-80
-90
θl
θr
θe
Ta
Tx
Tr
θi
θa
θo
0
10
t(mins)
20

FIG. 5

time t_o and heating was commenced at time t_i at which the temperature was θ_i. The rate of change of heating in the fore-period was given by $v_a = (\theta_o-\theta_i)/(t_i-t_o)\mu v.t^{-1}$ and the average temperature, $\theta_a = \frac{1}{2}(\theta_o-\theta_i)\mu v$. The heat change was given by a rise in e.m.f. from θ_i to θ_e, where θ_e marks the commencement of the after-rating period and θ_1 its termination, the corresponding times are t_e and t_1. The rate of cooling and the average temperature in this period were then, $v_r = (\theta_e-\theta_1)/(t_1-t_e)\mu v.t^{-1}$ and $\theta_r = \frac{1}{2}(\theta_e-\theta_1)$. The corrected temperature change was given by the Regnault-Pfaundler formula,

$$\Delta\theta = \theta_e - \theta_i + (t_e-t_i)v_a + (v_r-v_a)/(\theta_r-\theta_a)\left[\tfrac{1}{2}(\theta_e-\theta_i) + \sum_{t_i-1}^{t_e} -(t_e-t_i)\theta_a\right]$$

This method corrects for different gradients in the fore- and after-periods and also for the finite time for the experimental period.

The resistance of the heating element was measured by connecting a pair of wires from the heater to a potentiometer. The potential across the element was measured, before and after each experiment, with a known current flowing in the circuit.

The total amount of heat generated in the calorimeter during a heating period can be written,

$$\text{cals.} = I \times R^2 \times t \times 1/4.183.$$

where I is the current in amps, R is the resistance of the heater and t the duration of the current in

seconds. In these experiments 4.183 joules were taken as equivalent to 1 calorie.

Thermistor Calorimeter:-

The experimental procedure was essentially the same as described above. When the calorimeter had equilibrated the bridge was balanced and the chart recorder switched on. A vertical or near vertical trace was obtained which was horizontally displaced by heating or mixing periods. Since this calorimeter was much more sensitive, less electrical energy was used to find the energy equivalent and it was important that the current and its duration were measured very accurately. The on/off switch for the heater circuit was synchronised to start and stop an electronic timer and the duration of the heating current was measured to 1/1,000 sec. The experimental traces were analysed by Eitel's method. Energy equivalents were estimated before and after each mixing period.

CHEMICALS.

All graduated glassware used in volumetric work was Grade A and AnalaR reagents were used where available. All weights were corrected to vacuum. In all complexing experiments the metal ions were added as solutions of their chlorides and the carboxylate anions as solutions of their disodium salts.

Preparation of Zinc Chloride:-

To a weighed quantity of AnalaR zinc oxide was added a slight stoichiometric deficiency of concentrated AnalaR hydrochloric acid whose chloride content had been checked gravimetrically by precipitation of its silver salt. The solution was shaken until the reaction was complete, then filtered through a low porosity paper. A calculated volume of distilled water was added until the solution was approximately molar. The final pH was adjusted by addition of a known quantity of acid to avoid precipitation of the metal hydroxide. The solution was analysed for zinc by precipitation of the metal as its quinaldinate.[28]

Preparation of Nickel (II), Cobalt (II), and Manganese (II) Chlorides:-

Stock solutions of these metals were made with distilled water from the AnalaR salts. They were analysed for cation by passing portions through an ion exchange column, Amberlite IR - 120 (H^+ - form) and titrating the eluted acid with standard sodium hydroxide.

Preparation of Copper (II) Chloride:-

Solutions were prepared by a similar method to that for zinc chloride, starting with the AnalaR metal oxide. Solutions of cupric chloride were analysed by a redox titration with thiosulphate.[28]

Preparation of Disodium Malonate and Disodium Succinate:-

Reagent grade materials were recrystallised from distilled water and dried under vacuum. Solutions of the salt were analysed for cation in the manner described for nickel chloride.

Preparation of Standard Sodium Hydroxide Solutions:-

A saturated solution of sodium hydroxide was prepared from AnalaR pellets and distilled water. Standard solutions were made from carbonate free, boiled, distilled water and portions of the saturated stock solution. These solutions were stored in automatic burettes, whose outlets were effectively protected from atmospheric carbon dioxide by soda lime guard tubes, and analysed by titration against weighed portions of AnalaR potassium hydrogen phthalate.

CALIBRATION OF CALORIMETERS.

There are a number of chemical reactions with well authenticated heat changes which have been used to check the calibration of solution calorimeters. Among the most common are: the heat of solution of crystalline potassium chloride,[30] the heat of reaction of tris(hydroximethyl)amino-methane with hydrochloric acid [31] and the heat of ionisation of water. [14,17,32,34,35,36,37].

Calibration of Thermopile Calorimeter:-

The heat of solution of potassium chloride was used to test this calorimeter. Weighed amounts of AnalaR salt were sealed in the mixing device and were broken into a weighed amount of distilled water. Direct comparison with results from other workers is made difficult because of the wide variety of concentrations and temperatures used. Davies, Singer and Staveley [15] have corrected previous data to a standard dilution of 1:167, moles potassium chloride to moles water at 25 °C. In this study the results were corrected to Staveley's ratio using Rossini's tables.[38] The results are listed in Table(I.).

Table (I)

Run	Wt.KClgms	Wt.H_2Ogms	Q cals.	Δ Hk.cals.mole^{-1}
1	2.3487	1,181.39	13.17	4.21
2	2.9994	1,189.92	16.56	4.13
3	2.8924	1,172.04	15.92	4.12
5	2.9975	1,186.90	17.02	4.25

Mean $\Delta H = 4.18 \pm 0.05$ k.cal. mole.$^{-1}$

The mean value of 4.18 k.cal.mole^{-1} compares well with that of Staveley,[15] 4.184, and Rossini[38] 4.194 k.cal.mole.$^{-1}$

Calibration of Thermistor Calorimeter:-

The heat of ionisation of water was used to test this calorimeter. The classical method of determining ΔH for the reaction,

$$H^+ + OH^- \rightleftharpoons H_2O$$

is to measure the heat of neutralisation of a strong acid with a strong base. The values in literature refer to a variety of ionic strengths and temperatures. Rossini,[32] Pitzer,[14] and Kegeles[34] corrected these values to zero ionic strength and 25°C. Recently estimations were carried out at low ionic strength with a refined correction for heat of dilution.[39] It has been shown[17] that the ΔH^o value is independant of the salt formed in the acid-base reaction, an identical result having been obtained with hydrochloric and perchloric acids. In testing the calorimeter the heat changes have been limited to approximately the same as those expected in the subsequent experiment on complex formation.

Sodium hydroxide solutions were sealed in the mixing device and the experimental heat change measured when this was opened into a dilute acid solution contained in the Dewar flask. Precautions were taken to limit the contamination by carbon dioxide during these runs. A stoichiometric excess of base was used avoiding any heat effects from neutralisation of carbonate in the base. The results are given in Table (II).

Table (II).

Run	moles $H_2O \times 10^4$	-Q cal.	$-\Delta H_I$	δcal.	$-\Delta H_o$
3	4.176	5.47	13.10	38	13.06
4	4.176	5.56	13.31	32	13.27
5	3.132	4.15	13.25	32	13.23
6	3.132	4.12	13.12	32	13.08
7	3.132	4.33	13.83	33	13.80
8	3.132	4.28	13.68	32	13.64
9	4.176	5.54	13.27	36	13.23
10	4.176	5.57	13.34	36	13.30

Mean ΔH_o = -13.33 ∓ 0.20 k.cal. $mole^{-1}$

The mean of the values is comparable to that obtained by most workers, a summary of which appears in Table (III).

Table (III).

Heat of Ionization of Water.

Reaction.	$-\Delta H_o$ k.cal.$mole^{-1}$.	Ref.
HCl + NaOH	13.363	14
HCl + NaOH	13.320	35
HCl + NaOH	13.336	36
HCl + NaOH	13.356	15
$HClO_4$ + NaOH	13.334	37
$HClO_4$ + NaOH	13.335	17
HCl + NaOH	13.34	17
$HClO_4$ + NaOH	13.33	this work.

Determination of Heats of Complex Formation:-

For measurement of the heat of complex formation, the Dewar contained solutions of the metal salt. Solutions of the disodium salt of the carboxylic acid was added from the mixing device. All solutions added to the calorimeters were transferred under nitrogen. An energy equivalent was calculated before and after mixing. The pH of the solution was measured at the end of each run. (E.I.L. Direct Reading Meter Model 23A) The heat of dilution, of the same volume of the disodium salt of the carboxylic acid, when opened into a solution of the same ionic strength as that of the metal chloride, but without the metal present, was estimated for each run. The pH of these solutions was also measured.

RESULTS.

McAuley and Nancollas[40] measured the e.m.f. for the cells of the type,

$$H_2, Pt \mid H_2A, \quad NaOH, \quad MCl_2 \mid AgCl, \quad Ag.$$

and found that results could be satisfactorily interpreted for a range in concentration of the metal and succinate ions, in terms of two complexes $MHSuoc^+$ and MSuoc. In similar studies on nickel malonate[41] it was possible to choose conditions such that only the uncharged complex, MMal, predominated and other complexes could be justifiably neglected. This procedure was adapted in the calorimetric experiments.

The thermodynamic association constant for the complex formation is,

$$K = [MA] \Big/ [M^{2+}] [A^{2+}] f_2^2, \quad .....(4)$$

and the first and second dissociations of the dibasic acid may be written,

$$k_1' = [H^+] [HA^-] f_1^2 \Big/ [H_2A], \quad .....(5)$$

$$k_2' = [H^+] [A^{2-}] f^2 \Big/ [HA^-], \quad .....(6)$$

The basic equations are the total amount of acid,

$$m_1 = [H_2A] + [HA^-] + [A^{2-}] + [MA] \quad ...(7)$$

and the total concentration of the metal ion,

$$m_2 = \left[M^{2+}\right] + \left[MA\right] \quad \ldots\ldots\ldots\ldots(8)$$

The total concentration of complex can be written,

$$\left[MA\right] = m_1 - \left[H_2A\right] - \left[HA^-\right] - \left[A^{2-}\right],$$

or,
$$\left[MA\right] = T - \left[A^{2-}\right], \quad \ldots\ldots\ldots\ldots(9)$$

From equations (4) - (9)

$$Kf_2^2\left[MA\right]^2 - \left[MA\right]\left[1 - Kf_2^2(T + m_2)\right] + Kf_2^2 T m_2 = 0$$

$$\ldots\ldots\ldots\ldots(10)$$

The ionic strength can be written,

$$I = \left[H^+\right] + 2m_1 + 3\left[M^{2+}\right] + \left[A^{2-}\right].$$

A computer programme was written to calculate the species present in solution. The starting value of ionic strength was taken as $m_1 + m_2$ and in the first solution of the quadratic (10), T was taken as m_1. This approximate value of the complex MA was used to calculate, M^{2+} and A^{2-}. From the measured pH value and the dissociation constants k_1' and k_2' of the acid, the concentrations of H_2A and HA^- were calculated and substituted in the expression for T. An improved value of the ionic strength was obtained and successive approximations were made until the ionic concentrations were constant. The dissociation constants k_1' and k_2' for succinic, malonic, and oxalic acids are given in Table (IV).

Value of association constants, K, of the complexes are listed in Table (V).

Table (IV).

Acid	k_1'	k_2'	Ref.
Oxalic	5.36×10^{-2}	5.42×10^{-5}	42
Malonic	1.38×10^{-4}	6.90×10^{-6}	42
Succinic	6.21×10^{-5}	2.31×10^{-6}	43

Table (V).

Reaction.	K	Ref.
$Cu^{2+} + Ox^{2-}$	1.54×10^{6}	43
$Ni^{2+} + Mal^{2-}$	1.26×10^{4}	41
$Zn^{2+} + Mal^{2-}$	6.38×10^{3}	44
$Mn^{2+} + Succ^{2-}$	1.84×10^{2}	40
$Co^{2+} + Succ^{2-}$	1.65×10^{2}	40
$Ni^{2+} + Succ^{2-}$	2.21×10^{2}	40
$Cu^{2+} + Succ^{2-}$	1.65×10^{3}	45
$Zn^{2+} + Succ^{2-}$	2.94×10^{2}	this work.

The heat change, Q, measured on mixing the metal ion and the ligand was considered to consist of,

$$Q = q(1) + q(2) + q(3) + q(4) \text{ cal.}$$

Where q (1) was the contribution from the heat of complex formation, q (2) was the heat of dilution of the disodium salt of the acid and q (3) and q (4)

were the heat contributions from changes in the acid equilibria on forming the complex. The value of q (2) was obtained from a blank run carried out for each experiment. If the pH of the blank is known then the concentrations of all the acid species in solution can be calculated from equations (5) and (6) and the electroneutrality,

$$2\left[A^{2-}\right] + \left[HA^{-}\right] + \left[OH^{-}\right] = 2m_1 + \left[H^{+}\right]$$

The concentrations of the acid species, H_2A, HA^- and A^{2-}, in the complexing solution, were solved by the computer and the concentration differences between the blank and the final solution gave the small heat corrections q (3) and q (4) according to the equilibria,

		Ref.
$H_2Succ \rightleftharpoons H^+ + HSucc^-$,	$\Delta H_{diss} = -0.76$k.cal.mole^{-1}.	46
$H\ Succ^- \rightleftharpoons H^+ + succ^{2-}$,	$\Delta H_{diss} = -0.11$k.cal.mole^{-1}.	46
$H_2Mal \rightleftharpoons H^+ + HMal^-$,	$\Delta H_{diss} = -1.18$k.cal.mole^{-1}.	42
$HMal^- \rightleftharpoons H^+ + Mal^{2-}$,	$\Delta H_{diss} = -1.36$k.cal.mole^{-1}.	42

Knowing q (2), q (3) and q (4), the corrected heat change Q' represented the heat contribution from complex formation.

Knowing the concentration of the complex present in the calorimeter and the corrected heat change, Q' cal, the heat of formation, ΔH_I k.cal.mole^{-1}, was calculated at the ionic strength of the experiment. The thermodynamic value, ΔH_o, was obtained using the data of Austin.[47]

$$\Delta H_o = \Delta H_I + 2.303\ RT^2\ \frac{3}{2}\left(\frac{1}{D}\frac{dD}{dT} + \frac{1}{T}\right)\log f_2^2 \quad \ldots\ldots(11)$$

The values of D, the dielectric constant of water, were those of Akerlof .[48]
The results for the heats of formation of copper (II) oxalate, nickel (II), Copper (II) and zinc (II) succinate appear in Tables (VI) to (XIII).

Table (VI).

$\Delta\theta$ units	E.E.calunit^{-1}	-Qcal.	-Q'cal.
1.8	0.064	0.11	0.15
6.5	0.034	0.22	0.29
7.4	0.033	0.24	0.34
4.1	0.046	0.19	0.25
5.0	0.040	0.20	0.27

Table (VI).

Heat of Formation of Copper Oxalate at 25°C.

Molar concentrations in solutions of copper oxalate.

Run	$m_1 \times 10^3$	$m_2 \times 10^3$	$CuOx \times 10^3$
1	1.3877	3.1459	1.3865
2	2.7781	5.2481	2.7761
3	2.8387	5.3627	2.8368
4	2.1220	4.2759	2.1204
5	2.2039	4.4409	2.2022

Run	$I \times 10^2$ mole.l^{-1}	$-\Delta H_I$ k.cal.mole^{-1}	$-\Delta H_o$ k.cal.mole^{-1}
1.	0.8064	0.33	0.07
2	1.2978	0.33	0.00
3	1.3261	0.38	0.04
4	1.0718	0.37	0.06
5	1.1130	0.41	0.10

Mean $\Delta H_o = -0.05 \pm 0.03$ k.cal.mole^{-1}

Heat of Formation of Nickel Malonate at 25°C.

Run	$m_2 \times 10^3$	$m_3 \times 10^3$	$mMol \times 10^3$
1	[illegible]	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]
3	4.1264	6.6220	5.7509
4	5.2954	7.8723	6.8224
5	6.1636	7.7648	6.7529

1	[illegible]	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]
3	1.7146	1.45	1.80
4	2.0007	1.62	1.95
5	1.9811	1.36	1.73

Mean ΔH° = 1.88 ± 0.09 K.cal./Mole.

Table (VII).

Heat of Formation of Nickel Malonate at 25°C.

molar concentrations in solution of nickel malonate.

Run	$m_1 \times 10^3$	$m_2 \times 10^3$	NiMal $\times 10^3$
1	3.9236	6.2935	3.5553
2	3.9737	7.9674	3.6489
3	4.1284	6.6220	3.7509
4	5.2352	7.8725	4.8224
5	5.1636	7.7648	4.7299

Run	$I \times 10^2$ molel^{-1}	ΔH_I k.cal.mole^{-1}	ΔH_o k.cal.mole^{-1}
1	1.6352	1.56	1.90
2	2.1117	1.55	1.96
3	1.7169	1.45	1.80
4	2.0007	1.62	1.99
5	1.9811	1.36	1.73

Mean $\Delta H_o = 1.88 \pm 0.09$ k.cal.mole^{-1}.

Table (VII).

H_2Ogm.	$\Delta\theta$units	E.E.cal.unit^{-1}	Qcal.	Q$'$cal.
320.1	25.3	0.062	1.58	1.78
308.1	25.4	0.063	1.60	1.74
304.3	25.1	0.059	1.46	1.66
319.9	32.3	0.071	2.29	2.50
324.3	24.5	0.078	1.89	2.08

Table (VIII).

H_2Ogm.	$\Delta\theta\mu v.$	E.E.cal.μv^{-1}	Qcal.	Q'cal.
1,262.6	4.70	1.81	8.51	8.71
1,209.6	4.80	1.97	9.41	9.60
1,404.7	4.28	1.67	7.17	7.39
1,172.4	4.90	1.51	7.25	7.45
1,143.0	5.38	1.41	7.59	7.77

Table (VIII).

Heat of Formation of Zinc Malonate at 25°C.

molar concentrations in solutions of zinc malonate.

Run	$m_1 \times 10^3$	$m_2 \times 10^3$	ZnMal $\times 10^3$
4	3.6072	4.0618	2.6870
5	4.1052	4.6226	3.0957
9	2.0795	8.2637	1.8963
10	2.4914	7.8612	2.2581
11	2.5557	8.0641	2.3091

Run	$I \times 10^2$ mole.l^{-1}	ΔH_I k.cal.mole^{-1}	ΔH_o k.cal.mole^{-1}
4	1.2097	2.57	2.90
5	1.3616	2.56	2.90
9	2.3414	2.77	3.22
10	2.1995	2.81	3.25
11	2.2582	2.94	3.38

Mean $\Delta H_o = 3.13 \pm 0.18$ k.cal.mole^{-1}.

Table (IX).

H_2Ogm.	$\Delta\theta$units	E.E.cal.unit^{-1}	Qcal.	Q'cal.
301.7	4.25	0.120	0.51	0.87
294.9	3.35	0.099	0.38	0.93
331.4	6.10	0.102	0.62	0.99
279.5	8.30	0.081	0.67	1.04
314.1	7.80	0.088	0.69	1.05

Table (IX).

Heat of Formation of Manganese Succinate at 25°C.

molar concentrations in solution of manganese succ.

Run	$m_1 \times 10^3$	$m_2 \times 10^3$	MnSucc $\times 10^4$
2	5.1037	6.8552	9.9870
3	5.2186	7.0096	9.8959
4	4.6284	12.4341	13.3220
5	5.4610	14.6700	16.4691
6	4.8762	13.0993	13.8000

Run	$I \times 10^2$ mole l^{-1}	ΔH_I k.cal.mole^{-1}	ΔH_o k.cal.mole^{-1}
2	3.1354	2.89	3.38
3	3.1983	2.53	3.02
4	4.5677	2.26	2.82
5	5.3609	2.27	2.87
6	4.8063	2.42	3.00

Mean $\Delta H_o = 3.02 \pm 0.15$ k.cal.mole^{-1}.

Table (X).

H_2Ogm	$\Delta\theta_{\mu v.}$	E.E.cal.$\mu v.^{-1}$	Qcal.	Q'cal.
1,205.3	1.77	1.51	2.67	3.05
1,232.0	1.56	1.56	2.43	2.81
1,194.5	1.80	1.46	2.62	3.00
1,265.8	1.45	1.51	2.18	2.50
1,220.6	1.52	1.47	2.24	2.62

Table (X).

Heat of Formation of Cobalt Succinate at 25°C.

molar concentrations in solutions of cobalt succ.

Run	$m_1 \times 10^3$	$m_2 \times 10^3$	CoSucc $\times 10^4$
1.	4.3360	7.1390	9.0856
3	4.2430	6.3775	8.2887
5	4.0291	7.8797	9.0292
6	3.8061	6.8672	8.0111
7	3.9456	7.1027	8.4121

Run	$I \times 10^2$ mole.l^{-1}	ΔH_I k.cal.mole^{-1}	ΔH_o k.cal.mole^{-1}
1	3.0737	2.79	3.27
3	2.8449	2.75	3.22
5	3.2052	2.78	3.27
6	2.8760	2.47	2.94
7	2.9729	2.55	3.03

Mean $\Delta H_o = 3.15 \pm 0.13$ k.cal.mole^{-1}.

Table (XI).

H_2Ogm.	$\Delta\theta\mu v$	E.E.cal.μv^{-1}	Qcal.	Q'cal.
1,091.4	1.80	1.28	2.30	2.55
1,208.0	1.50	1.62	2.40	2.62
1,110.3	1.50	1.37	2.06	2.27
1,112.8	1.40	1.38	1.93	2.14
1,164.0	1.70	1.44	2.44	2.73
1,151.4	1.45	1.43	2.07	2.37

Table (XI).

Heat of Formation of Nickel Succinate at 25°C.

molar concentrations in solutions of nickel succ.

Run	$m_1 \times 10^3$	$m_2 \times 10^3$	NiSucc $\times 10^3$
1	3.3603	9.8928	1.0570
3	3.9370	9.8206	1.2013
4	3.1316	8.8796	0.9474
5	3.1278	7.6511	0.8968
6	4.4797	9.1286	1.3115
7	4.5302	8.6696	1.2688

Run	$I \times 10^2$ mole.l^{-1}	ΔH_I k.cal.mole^{-1}	ΔH_o k.cal.mole^{-1}
1	3.5463	2.21	2.72
3	3.6373	1.81	2.33
4	3.2175	2.16	2.65
5	2.8731	2.14	2.61
6	3.5549	1.79	2.30
7	3.4413	1.62	2.13

Mean $\Delta H_o = 2.46 \pm 0.20$ k.cal.mole^{-1}

Table (XII).

H_2O gm.	$\Delta\theta$ units	E.E. cal-unit^{-1}	ρ cal.	q' cal.
321.85	9.1	0.075	0.58	0.83
302.90	10.8	0.070	0.76	0.91
315.65	8.4	0.063	0.53	0.68
314.35	10.6	0.050	0.53	0.68

Table (XII).

H_2O gm.	$\Delta\theta$ units	E.E. cal. unit^{-1}	Qcal.	Q'cal.
321.85	9.1	0.075	0.68	0.83
302.90	10.8	0.070	0.76	0.91
315.65	8.4	0.063	0.53	0.68
314.35	10.6	0.050	0.53	0.68

Table (XII).

Heat of Formation of Copper Succinate at 25°C.

molar concentrations of solutions of copper succ.

Run	$m_1 \times 10^3$	$m_2 \times 10^3$	CuSucc $\times 10^4$
1	1.2062	3.7402	6.0596
2	1.2803	3.9704	6.9333
3	1.2332	2.5497	5.2245
4	1.2383	2.5601	5.0454

Run	$I \times 10^2$ mole.l^{-1}	ΔH_I k.cal.mole^{-1}	ΔH_o k.cal.mole^{-1}
1	1.2109	4.26	4.58
2	1.2718	4.33	4.66
3	0.8896	4.12	4.40
4	0.8976	4.29	4.58

Mean $\Delta H_o = 4.56 \pm 0.07$ k.cal.mole^{-1}.

Table (XIII).

H_2Ogm.	$\Delta\theta$ units	E.E.cal.unit^{-1}	Qcal.	Q'cal.
336.5	10.5	0.059	0.62	0.86
300.1	10.5	0.055	0.58	0.84
302.5	12.8	0.049	0.63	0.89
304.8	13.3	0.051	0.68	0.93

Table (XIII).

Heat of Formation of Zinc Succinate at 25°C.

Run	molar concentrations in solutions of zinc succ. $m_1 \times 10^3$	$m_2 \times 10^3$	ZnSucc $\times 10^4$
1	2.8607	3.8752	6.2758
2	3.1678	5.7216	7.3183
3	3.1435	5.6778	7.2774
4	3.1108	7.0234	8.0060

Run	$I \times 10^2$ mole.l^{-1}	ΔH_I k.cal.mole^{-1}	ΔH_o k.cal.mole^{-1}
1	1.7358	4.08	4.48
2	2.2946	3.83	4.27
3	2.2776	4.05	4.49
4	2.6441	3.84	4.31

Mean $\Delta H_o = 4.39 \pm 0.10$ k.cal.mole^{-1}.

PART II

Association in Solutions of Zinc Succinate.

The greater part of this thesis is devoted to the calorimetric determination of heats of complex formation at 25°C. Measurements have been made at low concentration so that a reliable estimate of the activity coefficients for all ionic species in solution could be made. The final result will reflect both the accuracy of the heat measurement and the value chosen for the association constant. In the case of zinc succinate systems there are no reliable equilibrium data at low ionic strength. Cannon and Kibrick [49] have studied this system at ionic strength 0.1, and showed that two complexes $MHSucc^+$ and $MSucc$ were present. Gelles and Hay [50] also estimated the association constant. The following cell was used to measure the e.m.f.s at 25°C.

H_2, Pt / $ZnCl_2$, NaOH, H_2Succ / AgCl, Ag.

CHEMICALS.

AnalaR succinic acid was used without further purification. Solutions of zinc chloride and sodium hydroxide were prepared as in Part I. The chloride content of the zinc solutions was estimated gravimetrically by precipitation of silver chloride. AnalaR hydrochloric acid was similarly analysed. Sodium hydroxide solutions were standardised against weighed portions of AnalaR potassium hydrogen phthalate. The hydrogen used in the cell was purified by a Deoxo purifier (Baker Platinum Division , Engelhard Industries Ltd., London.) and saturated with water vapour by passing through a series of bubblers.

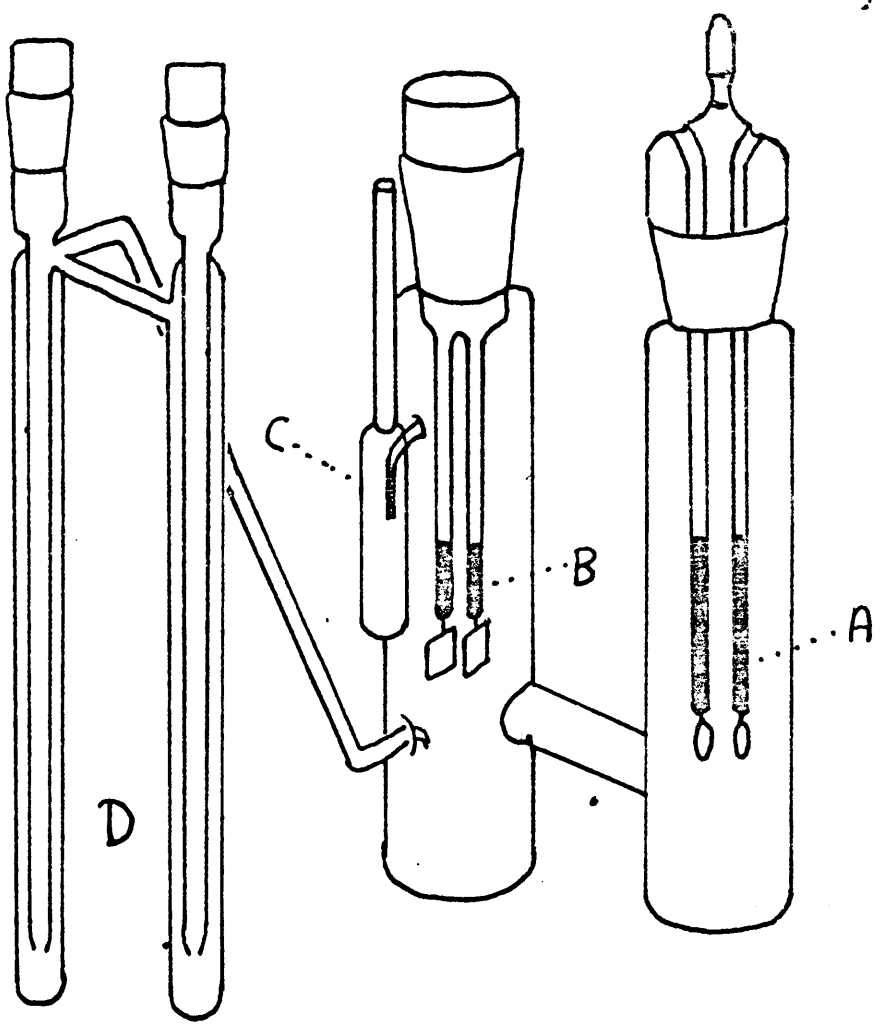
APPARATUS

The e.m.f.s were measured by a precision vernier potentiometer(Type 10, Croyden Precision Inst., Co. Croyden Surrey.) having a range from 1.9volts to 0.1 microvolts. A sensitive spot reflecting coil galvenometer was used (Cambridge Inst. Co. Ltd. London.) in conjunction with a lamp and a scale set at a distance of one metre. The potentiometer was standardised against a Weston cell (Cambridge Inst. Co. Ltd.) kept in an oil thermostat maintained at 25 $\pm$ 0.2^{o}C. E.m.f. cells were placed in a large water thermostat similar to that described in Part I.

The cell (Fig 6) employed was similar to that used by Noyes and Ellis.[51] Two hydrogen presaturators were made integral with the hydrogen electrode compartment, as was done by Harned and Morrison,[52] and the modifications of Ashby, Crooke and Dalta[53] were also incorporated. The cells were fitted with standard B29 ground glass sockets, and both electrodes were supported in ground glass cones. In each cell there were two silver, silver-chloride electrodes (A Fig 6) and two hydrogen electrodes (B Fig 6) so that ~~few~~ two estimates of the cell e.m.f. could be made. Leading from the hydrogen compartment was a guard tube (C Fig 6) and any liquid blown into this by the stream of hydrogen was immediately removed.

The silver, silver-chloride electrodes were of the thermal-electrolytic type as described by Harned.[54] A platinum wire about 5cm long was wound into a helix of 0.3cm diameter. One end of the platinum wire was sealed into a pyrex tube to be incorporated into the electrode contact. The helix was filled with a thick paste of spectroscopically pure silver oxide. (Johnston - Mathey and Co. Hatton Garden, London). After drying in an oven at 100°C the coils were heated in a muffle furnace to 400°C and held at that temperature until the decomposition of the oxide was complete. This process was repeated until an even coating covered the electrode. The platinum glass seal was made with a small amount of Araldite resin. The electrodes were chloridised in the absence of light by electrolysis in a solution of normal hydrochloric acid at an approximate current density of 2amps/cm^2 for two

THE E.M.F. CELL



A - Silver - Silver Chloride Electrodes.
B - Hydrogen Electrodes.
C - Guard Tube.
D - Presaturators.

FIG. 6

to three hours, using a platinum cathode. After preparation, the electrodes were stored in hydrogen saturated water for two to three weeks after which they were found to have a constant potential.

The hydrogen electrodes were constructed by welding a piece of platinum foil, 1cm by 2.5cm, on to a platinum wire which was then sealed into a pyrex glass tube to be attached to a B29 socket. The electrodes were cleaned in nitric acid, washed thoroughly in distilled water, then platinised in a solution containing 2.5°/o chloroplatinic acid in normal hydrochloric acid, for approximately five minutes at a current density of 0.2amps/cm^2, reversing the current every fifteen seconds. The platinum black coating was not sufficient to obscure the metallic surface of the electrode.

Determination of E_o for the Silver, Silver-Chloride Electrodes:-

Harned and Ehlers[55,56], have determined the standard electrode potential of the silver, silver-chloride electrode over a temperature range from 0° to 60°C. It has been shown[57] that there is difficulty in establishing an E_o value better than 0.2m.v, due to the small differences in the solid phase structure of each electrode, and it has been recommended that each worker standardises his own electrodes in 0.01 molal hydrochloric acid using an activity coefficient of 0.904 for γ_1 at 25°C.

Procedure for e.m.f. Measurement:-

Stock solutions of succinic acid and zinc chloride were stored in stoppered pyrex flasks. Weighed portions of these were transferred to 500ml Quickfit flasks for preparation of experimental solutions. Sodium hydroxide solutions were added from an automatic burette. A bubbler head was fitted to each flask such that the experimental solutions could be swept with hydrogen. Each cell was cleansed with chromic acid, washed thoroughly with distilled water and allowed to dry in an oven at 110°C. The cell was swept out with hydrogen and then filled with the experimental solution. The electrodes were washed with the experimental solution before being fitted into the cell. The complete cell was placed in the thermostat and hydrogen passed into the electrode compartment at a constant rate of 2-3 bubbles per second. Each cell was allowed to settle for about three hours before commencing e.m.f. readings. When readings had been constant for thirty minutes the barometric pressure and room temperature were noted and the recorded e.m.f.s were corrected for pressure. In making these corrections the effect of bubbler depth was ignored.[58]

RESULTS.

In measurements using the cell,

$$H_2, Pt/H_2Succ\ (m_1), NaOH\ (m_2), MCl_2(m_3),/\ AgCl,Ag.$$

if m_1, m_2 and m_3 are the molal concentrations of oxalic acid, sodium hydroxide and metal chloride, respectively, the corrected e.m.f. of the cell, E', and the standard potential of the silver, silver-chloride electrode, E^o, are combined in the relationship,

$$E' - E^o = 2.303\ RT/F \log a_{Cl^-}, a_{H^+}, \quad \ldots\ldots(12)$$

and the concentration of the hydrogen ions is given by rearrangement of this equation, (where $k = 2.303\ RT/F$).

$$-\log [H^+] = \frac{(E' - E^o)}{k} + 2\log m_3 + \log \gamma_{H^+}\gamma_{Cl^-} \quad \ldots\ldots(13)$$

The ionic concentrations of the species were obtained from the equations,

$$m_1 = [H_2Succ] + [HSucc^-] + [Succ^{2-}] + [MSucc] + [MHSucc^+] \quad \ldots\ldots(14)$$

$$m_3 = [M^{2+}] + [MHSucc^+] + [MSucc]. \quad \ldots\ldots(15)$$

electroneutrality,

$$\left[H^+\right] + 2\left[M^{2+}\right] + \left[MHSucc^+\right] + m_2 = \left[HSucc^-\right] + 2\left[Succ^{2-}\right] + 2m_3 \quad \ldots\ldots(16)$$

and the dissociation constants k_1' and k_2' of succinic acid. The thermodynamic association constants of the complexes may be written,

$$K = \frac{\left[MSucc\right]}{\left[M^{2+}\right]\left[Succ^{2-}\right]\gamma_2^2} , \quad \ldots\ldots(17)$$

$$K_1 = \frac{\left[MHSucc^+\right]}{\left[M^{2+}\right]\left[HSucc^-\right]\gamma_2} , \quad \ldots\ldots(18)$$

Equations (13) - (18) yielded the quadratic,

$$\left[HSucc^-\right]^2\left\{K_1\gamma_2\,\frac{(1-\left[H^+\right]\gamma_1^2)}{k_1'} + \frac{k_2'}{\left[H^+\right]\gamma_2}\right\}$$

$$+\left[HSucc\right]\left\{1+\frac{2\left[H^+\right]\gamma_2\gamma_1}{k_1'} + K_1(m_3-m_1)\gamma_2\right\} + m_2 + \left[H^+\right] - 2m_1 = 0 \quad \ldots\ldots(19)$$

The ionic strength can be written,

$$I = 3m_3 - m_1 + 4\left[Succ^{2-}\right] + \left[H_2Succ\right] + 2\left[HSucc^{-}\right],$$

and the activity coefficients obtained from the Davies Equation. (3). The thermodynamic association constants at 25°C were calculated on a KDF9 electronic computer. Values of K were obtained by inserting a series of values of K_1. When K_1 = 1 there was a large root mean square deviation for K, but as K_1 increased this passed through a minimum. The K_1 value which gave the smallest deviation was taken as the correct one. Table (XIV) summarises the data, the best K_1 value being 32.0 when K = 294. The e.m.f. data appears in Table (XV).

Table (XIV).

$K \times 10^{-2}$	K_1	RMS deviation.
2.10	1.0	8.63
2.34	10.0	7.95
2.62	20.0	7.41
2.75	25.0	7.26
2.83	28.0	7.20
2.86	29.0	7.19
2.88^7	30.0	7.18^5
2.91^3	31.0	7.18^0
2.94^1	32.0	7.17^6
2.96^7	33.0	7.17^6
2.99	34.0	7.18
3.02	35.0	7.19

Table (XV).

Molal concentrations in zinc succinate solutions.

	1	2	3	4
$m_1 \times 10^3$	3.8320	6.5192	3.9276	3.6495
$m_2 \times 10^3$	6.2166	10.9539	6.4900	6.0743
$m_3 \times 10^3$	6.7556	8.2814	7.0177	6.2751

Results using $K_1 = 32$.

Sol^n.	$K \times 10^{-2}$	$M^{2+} \times 10^3$	$MA \times 10^3$
1	2.8390	5.8477	0.7848
1	2.8430	5.8470	0.7855
2	2.8893	6.6533	1.4400
2	2.9430	6.6368	1.4568
3	2.9613	6.0272	0.8714
3	3.0408	6.0127	0.8862
4	2.9982	5.3806	0.7961
4	3.0106	5.3785	0.7983

Mean $K = 2.94 \times 10^2$.

Table (XV).

Results using $K_1 = 32.0$

$MHA^+ \times 10^4$	$HA^- \times 10^3$	$A^{2-} \times 10^3$	$I \times 10^2$
1.2303	1.2282	1.6495	2.5536
1.2302	1.2281	1.6488	2.5533
1.8811	1.7835	3.0525	3.4157
1.8772	1.7833	3.0360	4.4091
1.1908	1.1635	1.7338	2.6427
1.1882	1.1631	1.7193	2.6369
0.9832	1.0499	1.6681	2.3985
0.9828	1.0498	1.6662	2.3977

In calculations involving the ionic species in solution the ion pair $ZnCl^+$ was ignored since the association constant for this reaction has been estimated to be less than unity[59]. The low value found for K_1 compares well with 15 and 20, the association constants for the corresponding manganese and nickel complexes[40]. Gelles and Hay[50] found K to be 3.17×10^2 compared with 2.94×10^2 in this work.

A summary of all the thermodynamic data available for the transition metal complexes of oxalic, malonic and succinic acids is shown in Table (XVI). In this table the entropy change, ΔS, is calculated using the calorimetrically estimated enthalpy change, ΔH_C, where possible. ΔH_T refers to those heats obtained from temperature coefficients.

Table (XVI).

Transition Metal Dicarboxylates.

Oxalates (MOx).

Metal	ΔH_C	ΔH_T	$-\Delta G$	ΔS	Ref.
Mn	-	1.42	5.41	22.9	60
Co	-	0.59	6.54	23.9	60
Ni	-	0.15	7.05	24.2	60
Cu	-0.05	-	8.49	28.3	43

Malonates (MMal).

Metal	ΔH_C	ΔH_T	$-\Delta G$	ΔS	Ref.
Mn	3.68	3.53	4.48	27.4	41,61
Co	2.90	2.57	5.13	27.0	41,61
Ni	1.88	1.77	5.60	25.0	41
Cu	2.85	-	7.69	35.4	45
Zn	3.13	3.06	5.22	28.0	44

Succinates(MSucc).

Metal	ΔH_C	ΔH_T	$-\Delta G$	ΔS	Ref.
Mn	3.02	2.95	3.09	20.5	40
Co	3.15	2.81	3.02	20.7	40
Ni	2.46	2.23	3.20	19.0	40
Cu	4.56	-	4.42	33.5	45
Zn	4.39	-	3.36	26.0	

PART III

General Discussion.

DISCUSSION.

There are two methods of determining the thermodynamic association constant, K_T, for the reaction,

$$M^{2+} + A^{2-} \rightleftharpoons MA. \qquad \ldots\ldots(19).$$

In the first method the stoichiometric constant for the reaction is converted to the thermodynamic value using the ratio of the activity coefficients.

$$K_T = K_S \times \frac{f_{MA}}{f_{A^{2-}} f_{M^{2+}}} .$$

The second method involves the calculation of the stoichiometric association constant at a series of ionic strengths and obtaining K_T by extrapolating to zero.

It has been shown [62] for metal dicarboxylate complexes, the activity coefficients estimated from the Davies equation (3) allow an association constant to be calculated which is in excellent agreement with that obtained from the second method.

Harned and Robinson [63] substituted experimental mean activity coefficients for alkali halides into the Debye-Hückel equation (1) and calculated $\mathring{a}$ values. For caesium iodide the value of $\mathring{a}$, 2.78 $\mathring{A}$, is less than the sum of the crystal lattice spacing, 3.85 $\mathring{A}$ This result probably

reflects the uncertainties introduced into the Debye-Hückel theory through the assumption of purely electrostatic forces and it has been suggested[7] that short range quantum mechanical forces are superimposed on purely coulombic forces of attraction. W, the work done in forming an ion pair from separate ions in solution can be written,

$$W = \frac{\Delta G}{N} - kT \ln 55.5.$$

where N is Avogadros number and k isthe Boltzman constant. The term - kT ln 55.5 is introduced to make the work term unitary, representing a decrease in the number of solute particles by one unit. Its inclusion makes K dimensionless, 55.5 being the number of moles of water in 1,000 grams. The work term, W, may be considered to consist of two parts; $W_{Env.}$ representing the long range electrostatic forces which are independant of environment but will be broken by thermal agitation, and $W_{Non.}$ representing short range quantum mechanical forces which are independant of environment but will be broken by thermal agitation.

$$W = W_{Env.} + W_{Non.} = -kT\left[\ln K + \ln 55.5\right]$$

$$= -kT \ln K_x \quad \ldots\ldots\ldots(21).$$

The dependance of K values on these two quantities has been discussed by Davies [64]. He found that

a linear plot of log K versus z^2/r was obtained for the alkali and alkaline earth metal hydroxides. This was expected since both series of these metal ions have inert gas structure and the bonding would be predominately electrostatic. In this case the $W_{Env.}$ term is almost completely electrostatic and can be replaced by W_{El}, and assumed that it varies with the inverse of the bulk dielectric, D. For normal temperatures ($\sim 298^{o}K$) the inverse of the dielectric constant can be expressed by,

$$\frac{1}{D} = \frac{e^{T/\theta'}}{D_o} \quad ,$$

where D_o and θ' are constants for the chosen solvent. If $W_{El.}$ is proportional to 1/D then equation (21) will have the form,

$$\ln K_x = -c\left\{\frac{a + e^{T/\theta'}}{T}\right\}, \qquad \ldots\ldots(22)$$

where $ca = \frac{W_{Non}}{k}$ and $ce^{T/\theta'} = \frac{W_{El}}{k}$.

If equation (21) is differentiated with respect to temperature and equated to zero, then we have,

$$\frac{a}{T^2} + (1 - T/\theta')\frac{e^{T/\theta'}}{T^2} = 0 \qquad \ldots\ldots(23)$$

It can be shown that ln K_x will pass through a minimum at temperature T^* such that,

$$T^* = \theta'\left(1 + \frac{a}{e^{T^*/\theta}}\right),$$

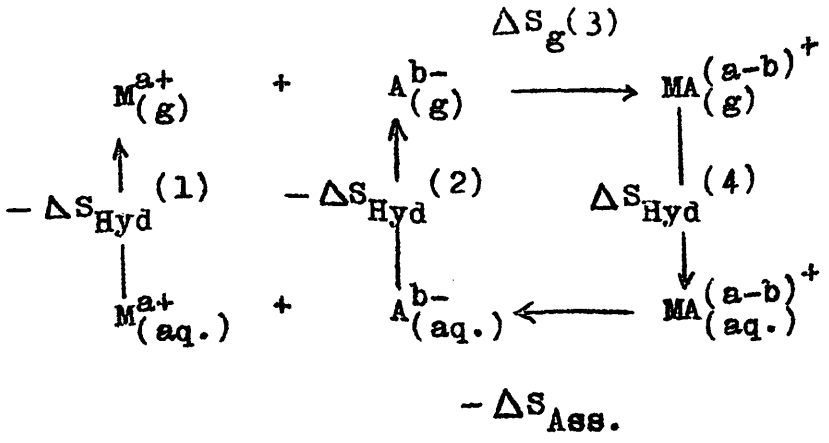
or

$$T^* = \theta'\left(1 + \frac{W_{Non}}{W_{El}^*}\right),$$

where W_{El}^* is the value of W_{El} at temperature T^*. The position of the minimum depending not on the sum, $W_{Non} + W_{El}$, but on their ratio.

If W_{El} is the predominant term then the position of T^* may be sufficiently low to be below the freezing point of the solvent and K will rise over the temperature range studied. In this case dlnK/dT is positive for the entire range, inferring a predominately electrostatic bond in the association. This behaviour is noted for the alkaline earth hydroxides. For the hydroxides of metal ions such as ferric, the W_{Non} term becomes dominant and it is possible that thermal effects could dissociate the ion pairs. MacAuley [65] calculated the temperature at which ΔH_o for the transition metal oxalates was zero and it was found to fall along the series Ni, Co and Mn. This possibly reflects the increasing b-type character with increasing atomic number in the first transition series.

An entropy cycle can be written for equilibrium, (19)



where $\Delta S_{Hyd}(1)$ is the entropy change accompanying the hydration of a gas phase cation and $\Delta S_{Hyd}(2)$ and $\Delta S_{Hyd}(4)$ are the corresponding values for the anion and the complex. $\Delta S_g(3)$ is the entropy change on association in the gas phase. The observed entropy of association can then be written,

$$\Delta S_{Ass} = \Delta S_{Hyd}(4) - \Delta S_{Hyd}(1) - \Delta S_{Hyd}(2) + \Delta S_g(3) \quad \ldots\ldots(25).$$

In the gas phase, the entropy change includes both rotational and translational terms.

$$\Delta S_g(3) = S_{trans}(MA^{(a-b)+}) + S_{rot}(MA^{(a-b)+}) - S_{trans}(M^{a+}) - S_{trans}(A^{b-}) - S_{rot}(A^{b-}) \quad \ldots\ldots(26).$$

S_{trans} for monatomic ions and diatomic molecules may be obtained from the Sackur-Tetrode equation which at 25°C has the form,

$$S_{trans.} = 1.5\ R\ \ln M + 26.03 \qquad .....(27),$$

where M is the atomic (or molecular) weight of the ion. For symmetrical non-linear anions, (eg.SO_4^{2-}), $S_{rot}(A^{b-})$ may be obtained from the equation,[66]

$$S_{rot}(A^{b-}) = 2.2868\ (3\log T + 3\log I_A - 2\log \sigma) + 267.52,$$

when I_A is the moment of inertia about the bonds and σ is the symmetry number. For an ion-pair which can be considered as a linear molecule,

$$S_{trans}\ (MA^{(a-b)+}) + S_{rot}\ (MA^{(a-b)+})$$

$$= 2.2868\ (7\log T + 3\log M + 2\log I_B - 2\log \sigma) - 6.661 \qquad .....(28),$$

where I_B is the moment of inertia about its axis. For rigid molecules which are not linear, the equation used is,

$$S_{trans}(MA^{(a-b)+}) + S_{rot}(MA^{(a-b)+})$$

$$= 2.2868(8\log T + \log I_A I_B I_C + 3\log M - 2\log \sigma) - 7.697 \qquad .....(29).$$

In the case of oxalate, malonate and succinate the ions were assumed to be planar and the inter-atomic distances used in calculation were those of the solid phase[67]. Values of the entropies of the free ions, required in the calculation of $\Delta S_{Hyd}(1)$ and $\Delta S_{Hyd}(2)$ were obtained from Latimer[68] except in the case of nickel and cobalt where Staveley's[69] value of S^{o}_{aq} were taken. To evaluate $\Delta S_{Hyd}(2)$, known values of ΔS_{Hyd} for a series of divalent anions were plotted against the reciprocal of their hydrated anionic radius, r^{-1}_{Hyd}. The latter were obtained from the formula of Jenkins and Monk[70],

$$r_{Hyd} = 9.16 \times 10^{-7} z / \Lambda^{o}_{i} ,$$

where Λ^{o}_{i} is the limiting ionic mobility of the ion. $S_g(A^{2-})$ was found using the Sackur-Tetrode equation, for SO_4^{2-}, CO_3^{2-}, SeO_4^{2-}, SO_3^{2-} and $S_2O_3^{2-}$ ions, their corresponding conductivity data were obtained from reference (71) to (75). Values of $\Delta S_{Hyd}(2)$ were interpolated from this plot for oxalate, malonate and succinate using their corrected hydrated radii[76,77].

Substitution of entropy data in equation (25) gave $\Delta S_{Hyd}(MA)$, the hydration entropy of the ion-pair. Entropy data are given in Table (XVII).

Table (XVII).

Complex	$S_g(MA)$	$\Delta S_{Ass.}$	$-\Delta S^{(4)}_{Hyd}$	$r_+^{-1}{}^{o}_{A}{}^{-1}$
MnOx	70.0	22.9	54.8	1.28
CoOx	70.0	23.9	55.8	1.35
NiOx	70.0	24.3	56.1	1.37
CuOx	70.0	28.3	52.5	1.39
MnMal	69.9	27.4	57.3	1.28
CoMal	70.3	27.0	59.8	1.35
NiMal	70.2	25.0	62.8	1.37
CuMal	70.3	35.4	52.6	1.39
ZnMal	70.3	28.0	61.6	1.39
MnSucc	70.5	20.5	64.2	1.28
CoSucc	70.6	20.7	65.9	1.35
NiSucc	70.6	19.0	68.7	1.37
CuSucc	70.7	33.5	55.5	1.39
ZnSucc	70.7	26.0	64.3	1.39

The hydrational entropies for the three anion groups have the following order, oxalate > malonate > succinate. If the five membered chelates have the most favourable configuration then charge neutralisation will be most effective for the oxalates, leading to a more positive entropy of hydration. In both the malonates and the succinates the more positive $\Delta S^{(4)}_{Hyd}$ value for copper(II) can be explained by an increase in co-valency in the metal-ligand bond.

In equation (19) the formation of the complex decreases the number of particles and the loss of translational energy could be expected to have a negative contribution to the overall entropy change, c.f. a gas phase reaction. If a more complete equation is written which includes solvation of the cation,

$$M^{2+}(H_2O)_n + A^{2-} \rightleftharpoons MA(H_2O)_{n-2} + 2H_2O \quad ,$$

then the replacement of two water molecules in the co-ordination sphere of the metal by one bidentate ligand molecule will have a positive entropy contribution. Frank and Evans[78] have proposed three different structural regions in the neighbourhood of a ion in solution. The first region being the primary hydration sphere, which in the case of the transition metals may be thought to contain a fixed number of water molecules, their number being limited by a packing or steric effect and the screening effect which causes a sharp decrease im field strength[79]. These water molecules are considered to have lost their translational freedom. Since coulombic forces are of a long range nature, there will be a second region in which the water molecules lose some of their translational freedom but are orientated by the ionic field with loss of rotational freedom. Frank[78] found that, although both these effects produced a negative entropy contribution,

experimental results from heats of evaporation from ionic solutions indicated that a third factor was present acting in the opposite sense. This was considered to be a contribution from a region outside the secondary hydration sphere in which the quasi-crystalline water structure is randomised by the non-polar effects of the ion. When two ionic species combine there will be a reduction in ionic field effects. In the 1:1 dicarboxylate complexes this will result in a neutral molecule, consequently entropy changes will be large and positive. The values obtained for the entropies of association lie between 20 and 30 cal.deg.$^{-1}$mole^{-1} (Table XVI), this being comparable to the values obtained for the sulphates[80] of nickel(II), cobalt (II) and manganese(II), which are 21.7,16.6 and 22.6, cal.deg.$^{-1}$mole^{-1}, respectively.

In forming chelated complexes there is a more positive entropy contribution than would be found from the same number of unidentate ligands. This can be explained by the unfavourable entropy of translation in the latter. An example of this is the nickel complexes of amonnia and ethylene-diamine [81],

$$Ni^{2+}_{aq} + 6NH_3 \rightleftharpoons Ni(NH_3)^{2+}_6 + xH_2O,\ \Delta S = -22 e.u.$$

$$Ni^{2+}_{aq} + 3en \rightleftharpoons Ni(en)^{2+}_3 + xH_2O,\ \Delta S = -2 e.u.$$

This has been called the chelate effect and is often used to explain the greater stability of chelates over their related non-chelated complexes. Some workers [82] have suggested that there is an entropy contribution of approximately 8 e.u. per chelate, but this must be an extremely qualitative figure.

In the transition metals it is accepted that the divalent ions are octahedrally co-ordinated with respect to water. In forming the uncharged 1:1 complex two water molecules would leave the co-ordination sphere of the metal ion to be replaced by the bidentate ligand. If the metal changed its co-ordination number from six to four, on forming the complex, then additional water molecules would be freed. This is quite possible for copper(II) and zinc(II) both of which favour tetrahedral structures and in the case of zinc(II) ultrasonic studies[83] have provided evidence for the existence of the species $Zn^{2+}(H_2O)_4$ as the hydrated cation. In the hexaquo complex of copper(II) the six co-ordination sites are not equivalent. The octahedral symmetry is disturbed such that there are two ligand sites, corresponding to the d_{z2} orbital, at which the metal-water bonds are longer. The molecule can be pictured as continually interchanging these weak bonds, this is supported by the high rates of substitution found for reactions with $Cu(H_2O)_6^{2+}$. In Table (XVI) it is seen that the entropy of association of both copper(II) malonate and succinate is much greater than that for the other metal ions. This could be explained

by the preference of copper to form tetrahedral complexes. Similarly, the high ΔS values for zinc succinate could also be attributed to the change in co-ordination number on forming the dicarboxylate complex.

The enthalpy changes observed for the 1:1 transition metal dicarboxylates are endothermic with the exception of copper oxalate which has a very small exothermic heat. If the metal-ligand bond is predominately electrostatic then an endothermic heat of formation is expected. For any one anion the exothermicity increases from manganese(II) to nickel(II) and then falls off to copper(II) and zinc(II).

A widely held explanation for the characteristic maximum obtained in enthalpy estimations for complexes of the first row transition series involves the crystal field theory. In an octahedral complex the effects of the ligands on the 'd' orbitals of the metal ion is to destroy the five-fold degeneracy such that they are no longer of equal energy. The division is into two levels, the higher, t_{2g}, containing the d_{z^2} and $d_{x^2-y^2}$ orbitals, the lower, e_g, consisting of the d_{xy}, d_{xz}, and d_{yz} orbitals. The energy separation between them being denoted by Δ. The crystal field stabilisation energy can be written as,

$$E = \frac{1}{5} (2nt_{2g} - 3ne_g)(Ee_g - Et_{2g}) ,$$

where n is the number of electrons in that level. It can be seen that this will be a maximum for

high-spin complexing when ions have 3 or 8 d-electrons. For divalent ions these maxima occur at vanadium and nickel. It is known that if the heats of hydration of the first row divalent transition metal ions are corrected for crystal field effects [84] then they lie on a smooth curve rising steadily through titanium(II), manganese(II) and zinc(II). These metal ions have 0, 5, and 10 d-electrons, respectively, each constituting a spherically symmetrical distribution of electrons which is not subject to crystal field effects. The crystal field splitting already discussed is only for an octahedral field; if the ligand field was tetrahedral then the splitting would be much less [85] and relative heat values for the tetrahedral complex would be more endothermic. Thus the tetrahedral complexes of copper and zinc could be relatively less stabilised than the octahedral complexes of the rest of the metal ions. Values of Δ, $Ee_g - Et_{2g}$, are estimated from spectroscopic measurements and it is noted that ligands with the greatest crystal field splitting effect are far removed from water in the spectrochemical series, whereas the anions, oxalate, malonate, and succinate are very close to water. This is probably due to the oxygen donor atom of the carboxylate group being akin to the oxygen of the water molecule. Since there is little difference in Δ, between ligand and water, it is possible that the crystal fields produced on complexing are very similar to those of the aquo ion.

From the enthalpy measurements carried out on the series of transition metal ions there is evidence to support the theory of increasing stability of the tetrahedral state over the octahedral state with increasing atomic number. This agrees with recent work on transition metal co-ordination.[86] This preference for the tetrahedral complex is probably due to the increased covalence in metal-ligand bonds of the tetrahedral complex as the electron affinity of the bivalent metal ion increases and this effect will become more apparent as the polarisability of the ligand increases.[87]

PART IV.

Monothiocyanate Complexes.

Metal Monothiocyanate Complexes.

A considerable number of complexes of thiocyanate and metal ions have been reported,[10] and the former's complexing ability has led to its use as a reagent in qualitative and quantitative analysis.[28] The thiocyanate ion exhibits linkage isomerism, bonding to the metal ion either through its sulphur or nitrogen atom. The former are correctly named thiocyanates and the latter are isothiocyanates. In this part of the thesis the complexes will all be called thiocyanates and bonding conditions discussed.

Experimental conditions were chosen such that the only complex present was the 1:1 complex, $MCNS^+$. The work was carried out at low concentrations so that the activity coefficients could be estimated from some extended form of the Debye-Hückel equation (3). It was hoped that the enthalpy changes would yield information concerning the donor atom of the ligand and to this end some I.R. measurements were made of the carbon nitrogen stretch frequency.

MATERIALS.

In all the estimations of the heat of formation of the thiocyanate complexes the ligand was added as a solution of its AnalaR ammonium salt. Complexing between manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), lead(II) and cadmium(II) with thiocyanate anion have been studied. With the exception of cadmium, the metal was prepared as its perchlorate.

Manganese(II) Perchlorate was prepared from the AnalaR metal chloride. The insoluble carbonate was precipitated from its chloride solution by addition of AnalaR sodium carbonate. This salt was filtered, washed and centrifuged repeatedly until free from chloride. The cation content was estimated on an Amberlite IR-120 (H^+form) cation exchange column. The eluted perchloric acid was filtered against standard base.

Cobalt(II) Perchlorate was prepared from the AnalaR chloride by addition of excess concentrated perchloric acid. Cobaltous perchlorate crystallised out from the solution. The crystals were washed with small volumes of distilled water until washings gave a negative chloride test. Solutions of cobalt(II) perchlorate were made with distilled water and the cation content estimated by complexiometric titration with EDTA. using Xylenol Orange as indicator.[28]

Nickel Perchlorate was prepared by the action of AnalaR perchloric acid on excess metal carbonate (B.D.H. Reagent Grade).

The resulting solution was filtered and the cation content estimated as for manganese perchlorate.

Copper(II) and Zinc(II) Perchlorates were prepared by adding to AnalaR perchloric acid, a slight excess of the appropriate metal oxide. The reaction flask was then shaken for about two hours before filtering the solution through a low porosity paper.

Solutions of cupric perchlorate were analysed volumetrically by a redox titration with thiosulphate.[28]

Zinc solutions were analysed by a complexiometric titration with EDTA, using Eriochrome Black T as an indicator[28]. A known small excess of perchloric acid was added to these solutions to prevent hydrolysis.

Lead Perchlorate was prepared from the AnalaR metal nitrate according to Willard and Kessner[88]. A 1% stoichiometric excess of AnalaR perchloric acid was diluted with a little water and added to the metal nitrate. The solution was heated to remove the nitric acid and evaporation stopped when fumes of perchloric acid were given off. The cation content was estimated by complexiometric titration with EDTA using Xylenol Orange as indicator [28].

A crystalline sample of lead thiocyanate was prepared by adding lead perchlorate solution to a concentrated solution of ammonium perchlorate from which the lead salt, $Pb(CNS)_2$, precipitated readily. The crystals were filtered, washed with water, then ether before being dried in a vacuum dessicator. The cadmium salt was prepared in an analagous manner except that crystals of $Cd(CNS)_2$ were obtained only after chilling the solution.

For each metal ion a solution was made with ammonium thiocyanate such that the metal:thiocyanate ratio was 2:1, and the ionic strength approximately 0.2mole.l^{-1}. These solutions were used in I.R. analysis of the CN stretch.

Experimental Procedure.

The calorimetric procedure was as described in Part I for the thermistor calorimeter. The solutions containing the metal ions were added to the distilled water in the Dewar vessels and the thiocyanate solution was added as the AnalaR ammonium thiocyanate from the mixing device. For all experimental runs the ionic strength was less than 5 x 10^{-2}mole.l^{-1}. Blank experiments were carried out in order to determine the heats of dilution, under the same conditions, of small volumes of ammonium thiocyanate into solutions of the same ionic strength but containing no metal ion. At the concentrations used in these experiments hydrothiocyanic acid is considered to be completely dissociated.

Spectra were recorded on a Unicam S.P. 100 double-beam infra-red spectrophotometer with an S.P. 130 sodium chloride prism-grating double monochromator.

Aqueous solutions of the thiocyanate complexes were examined in the CN stretch region, 1,900-2,200cm^{-1}. Solutions were contained in calcium fluoride cells having a path length of 0.04mm.

Nujoll mulls of solid lead and cadmium thiocyanate were prepared and the spectra recorded in the CS region, 700 - 900cm^{-1}.

Results and Discussion.

The thermodynamic equilibrium constant for the formation of the complex $MCNS^+$ can be written,

$$K = \frac{\left[MCNS^+\right]}{\left[M^{2+}\right]\left[CNS^-\right] f_2} \qquad \ldots\ldots\ldots(30).$$

The total concentration of the ligand, m_1, is given by,

$$m_1 = \left[MCNS^+\right] + \left[CNS^-\right] , \qquad \ldots\ldots\ldots(31),$$

and the total concentration of the metal ion m_2, is,

$$m_2 = \left[MCNS^+\right] + \left[M^{2+}\right] \qquad \ldots\ldots\ldots(32).$$

Substituting in equation (30) for M^{2+} and CNS^- ,

$$Kf_2 \left[MCNS^+\right]^2 - (1+(m_1+m_2)\, Kf_2)\left[MCNS^+\right] + m_1 m_2 Kf_2 = 0 \qquad \ldots\ldots\ldots(33).$$

The ionic strength is,

$$I = m_1 + m_2 + 2\left[M^{2+}\right] .$$

A starting value of the ionic strength was taken as $m_1 + m_2$. Solution of the quadratic in $MCNS^+$ allowed a first approximation for M^{2+} to be obtained from equation (32). An improved value for the ionic strength was then available and the activity coefficients calculated from

the Davies equation (3). A computer programme was devised to calculate all species present in solution and successive approximations were made in the ionic strength expression until a constant value was obtained.

The heats of formation at the experimental ionic strength were converted to the thermodynamic value, ΔH_o, using the same expression as in Part I, Equation (11). No heat change was detected on dilution of the ligand. The association constants for the complexing reactions were all estimated by spectrophotometry[10] and are shown below.

Reaction	K	Ref.
$Mn^{2+} + CNS^-$	17.0	89
$Co^{2+} + CNS^-$	52.3	90
$Ni^{2+} + CNS^-$	57.8	90
$Cu^{2+} + CNS^-$	212.7	90
$Zn^{2+} + CNS^-$	71.4	91
$Cd^{2+} + CNS^-$	322.0	92
$Pb^{2+} + CNS^-$	12.4	93

The results of the heat measurements appear in Tables (XVIII) to (XXIV) and the calculated ΔG and ΔS values appear in Table (XXV).

Table (XVIII).

Heat of Formation of Manganese Monothiocyanate at 25°C.

molar concentrations in solutions of manganese thiocyanate.

$m_1 \times 10^3$	$m_2 \times 10^3$	$MCNS^+ \times 10^4$	H_2O gm.
5.954	12.002	5.03	326.23
5.954	12.001	5.03	326.27
6.092	9.823	4.44	318.87
6.464	10.423	4.91	300.53
3.697	9.936	2.82	315.27

$I \times 10^2$ mole.l^{-1}	-Qcal.	$-\Delta H_I$ k.cal.mole^{-1}	$-\Delta H_o$ k.cal.mole^{-1}
4.0954	0.20	1.23	0.95
4.0949	0.20	1.21	0.94
3.4571	0.15	1.06	0.80
3.6749	0.15	1.04	0.78
3.2940	0.20	1.40	1.15

Mean $\Delta H_o = -0.92 \pm 0.11$k.cal.mole^{-1}.

Table (XIX).

Heat of Formation of Cobalt(II) Monothiocyanate at 25°C.

molar concentrations in solutions of cobalt thiocyanate.

$m_1 \times 10^3$	$m_2 \times 10^3$	$MCNS^+ \times 10^4$	H_2O gm.
3.605	5.545	4.71	323.24
4.092	6.294	5.78	284.85
3.580	5.507	4.66	325.56
4.268	6.566	6.18	273.06

$I \times 10^2$ mole.l^{-1}	-Qcal.	$-\Delta H_I$ k.cal.mole^{-1}	$-\Delta H_o$ k.cal.mole^{-1}
2.0680	0.28	1.87	1.66
2.3389	0.32	1.93	1.72
2.0543	0.28	1.86	1.66
2.4359	0.29	1.72	1.52

Mean ΔH_o = -1.63 $\pm$ 0.06k.cal.mole^{-1}.

Table (XX).

Heat of Formation of Nickel Monothiocyanate at 25°C.

molar concentrations in solutions of nickel thiocyanate.

$m_1 \times 10^3$	$m_2 \times 10^3$	$MCNS^+ \times 10^4$	H_2O gm.
3.726	7.688	6.35	326.66
4.314	8.901	7.97	282.14
2.445	5.044	3.15	298.70
4.191	8.648	7.62	290.40

$I \times 10^2$ mole.l^{-1}	-Qcal.	$-\Delta H_I$ k.cal.mole^{-1}	$-\Delta H_o$ k.cal.mole^{-1}
3.2589	0.52	2.51	2.26
3.7608	0.54	2.40	2.15
2.4679	0.24	2.59	2.37
3.6563	0.56	2.51	2.25

Mean $-\Delta H_o = 2.26 \pm 0.05$ k.cal.mole^{-1}.

Table (XXI).

Heat of Formation of Cupric Monothiocyanate at 25°C.

molar concentrations in solutions of copper thiocyanate.

$m_1 \times 10^3$	$m_2 \times 10^3$	$MCNS^+ \times 10^3$	H_2O gm.
4.019	6.710	1.475	302.80
3.918	6.540	1.423	310.63
2.544	4.248	0.747	286.97
2.371	3.959	0.674	307.90

$I \times 10^2$ mole.l^{-1}	-Qcal	$-\Delta H_I$ k.cal.mole^{-1}	$-\Delta H_o$ k.cal.mole^{-1}
2.8825	1.41	3.16	2.92
2.8128	1.36	3.08	2.84
2.8140	0.70	3.27	3.06
2.0402	0.69	3.35	3.14

Mean ΔH_o = -2.99 ± 0.11 k.cal.mole^{-1}.

Table (XXII).

Heat of Formation of Zinc(II) Monothiocyanate at 25°C.

molar concentrations in solutions of zinc thiocyanate.

$m_1 \times 10^3$	$m_2 \times 10^3$	$MCNS^+ \times 10^4$	H_2Ogm.
2.988	5.448	4.79	326.74
3.789	6.909	7.03	322.05
3.742	5.457	5.87	326.18

$I \times 10^2$ mole.l^{-1}	Qcal.	ΔH_I k.cal.mole^{-1}	ΔH_o k.cal.mole^{-1}
2.5462	0.00 ± 0.03	0.00 ± 0.20	0.22 ± 0.20
3.0302	0.00 ± 0.03	0.00 ± 0.20	0.23 ± 0.20
2.6040	0.00 ± 0.03	0.00 ± 0.20	0.22 ± 0.20

Mean ΔH_o = 0.22 ± 0.20 k.cal.mole^{-1}

Table (XXIII).

Heat of Formation of Cadmium(II) Monothiocyanate at 25°.

molar concentrations in solutions of cadmium thiocyanate.

$m_1 \times 10^3$	$m_2 \times 10^3$	$MCNS^+ \times 10^3$	H_2Ogm.
5.170	8.652	2.638	300.61
5.122	8.573	2.607	303.38
3.693	8.241	1.940	315.64
3.757	8.384	1.984	310.23
5.011	16.774	3.315	310.13
5.034	16.850	3.333	308.71

$I \times 10^2$ mole.l^{-1}	-Qcal.	$-\Delta H_I$ k.cal.mole^{-1}	$-\Delta H_o$ k.cal.mole^{-1}
2.5849	0.72	0.91	0.69
2.5627	0.82	1.04	0.84
2.4536	0.57	0.93	0.68
2.4939	0.54	0.87	0.66
4.8701	0.99	0.96	0.68
4.8916	0.91	0.88	0.59

Mean ΔH_o = -0.69 ± 0.05k.cal.mole^{-1}.

Table (XXIV).

Heat of Formation of Lead(II) Monothiocyanate at 25°C.

molar concentrations in solutions of lead thiocyanate.

$m_1 \times 10^3$	$m_2 \times 10^3$	$MCNS^+ \times 10^4$	H_2O gm.
4.929	10.048	2.80	306.31
4.943	10.076	2.81	305.42
5.876	19.165	5.16	315.62
5.867	19.136	5.15	316.08
5.919	19.305	5.22	313.09
5.849	19.079	5.13	317.11

$I \times 10^2$ moles.l^{-1}	Qcal.	ΔH_I k.cal.mole^{-1}	ΔH_o k.cal.mole^{-1}.
3.4512	0.00 ± 0.02	0.00 ± 0.20	0.25 ± 0.20
3.4610	0.00 ± 0.02	0.00 ± 0.20	0.25 ± 0.20
6.2338	0.00 ± 0.02	0.00 ± 0.10	0.32 ± 0.10
6.2245	0.00 ± 0.02	0.00 ± 0.10	0.32 ± 0.10
6.2789	0.00 ± 0.02	0.00 ± 0.10	0.32 ± 0.10
6.2059	0.00 ± 0.02	0.00 ± 0.10	0.32 ± 0.10

Mean ΔH_o = 0.30 ± 0.13 k.cal.mole^{-1}.

Table (XXV).

Thermodynamic Parameters of Monothiocyanate Complexes.

Metal	$-\Delta G$ k.cal.mole^{-1}	$-\Delta H$ k.cal.mole^{-1}	ΔS cal.deg.$^{-1}$mole^{-1}
Mn.	1.68	0.92	2.6
Co.	2.34	1.63	2.4
Ni.	2.40	2.26	0.5
Cu.	3.17	2.99	0.6
Zn.	2.53	-0.22	9.2
Cd.	3.42	0.69	9.2
Pb.	1.49	-0.30	6.0

It can be seen from Table (XXV) that all the enthalpies are small and in the case of two metals, zinc and lead, no heat change could be detected. In these cases the value of Q, the heat change, was taken as $0 \pm$ the experimental accuracy.

The heats of formation of the transition metal complexes increase from manganese to copper then there is a fall to zinc. This order is generally followed when the metal-ligand bond is predominately covalent and it parallels the variation in the second ionisation potential for the metal ion, $Mn < Co < Ni < Cu > Zn$. In the monothiocyanate complexes the abnormal endothermicity for zinc may reflect the elimination of extra water molecules and there may be a change in co-ordination from

the aquo-ion to the complex. This is supported by the high entropy change, 9.2cal.deg.$^{-1}$mole^{-1}. The heat value for the cadmium complex, ΔH = -0.59k.cal.mole^{-1}, is more exothermic than that for the zinc complex, ΔH = 0.22k.cal.mole^{-1}, probably due to the increased covalency of the former. A similar enthalpy relationship between the zinc and cadmium EDTA complexes was found by Staveley[15].

Entropy changes for the transition metal complexes are small and favourable. A large entropy change would not be expected since the final complex is charged and will thus retain some of its solvent ordering properties. Table (XXVI) contains thermodynamic data for the transition metal ethylenediamine complexes and a fair comparison can be made with the thiocyanates.

Table (XXVI).

Reaction	$-\Delta G$ k.cal.mole^{-1}	$-\Delta H$ k.cal.mole^{-1}	ΔS cal.deg.$^{-1}$mole^{-1}	Ref.
Mn^{2+} + en	3.75	2.80	3.0	94,95
Co^{2+} + en	8.10	6.90	7.0	96,95
Ni^{2+} + en	10.50	8.90	5.5	96,95
Cu^{2+} + en	14.60	13.00	5.4	97
Zn^{2+} + en	7.90	6.65	4.0	98,95

Both groups of complexes have the same pattern of changes in ΔH. The entropy term in the Men^{2+} complex is higher than in the corresponding

thiocyanate, because the chelate effect outweighs the difference of the additional unit of charge.

There is little data available for direct comparison with the transition metal monothiocyanates. An attempt has been made to calculate ΔH for the nickel complex, $NiCNS^+$, by Mohapatra[99], using the association constants at two temperatures. The value at 25°C, 3.15×10^2, was calculated from e.m.f. data and the value at 35°, 1.52×10^2, found by spectrophotometry. At 25°C, the following thermodynamic parameters were reported, $\Delta G = -2.05$ k.cal.mole^{-1}, $\Delta H = -13.17$k.cal.mole^{-1} and $\Delta S = 51.1$cal.deg.$^{-1}$mole^{-1}. It seems most unlikely that such a high entropy is correct. From the association constants dlnK/dT is negative thus ΔH is exothermic but the entropy change must be unfavourable since $-\Delta H > -\Delta G$. On recalculating Mohapatra's data $\Delta G = -3.40$k.cal.mole^{-1}, $\Delta H = -12.91$ k.cal.mole^{-1} and $\Delta S = -31.8$cal.deg.$^{-1}$mole^{-1}. This illustrates the inaccuracies which can arise from enthalpies calculated from a limited study of association constants.

A similar study on lead monothiocyanate [93], using the association constants at two temperatures, gave a value for the heat of association as, $\Delta H = -0.6$k.cal.mole^{-1}, whereas the value found in this work was endothermic, $\Delta H = 0.30$k.cal.mole^{-1}.

In organic nitriles the CN stretching frequency is usually about 2,250cm^{-1}. Whilst in all thiocyanate complexes and free anions in solution there is a shift to lower frequencies. The CS stretch recorded in mercaptans[15] in the region of 600-700cm^{-1} in comparison with 700-800cm^{-1} in thiocyanate complexes. These frequency changes have been attributed to loss of triple bond character in the CN stretch and gain in double bond character in the CS stretch.[100] Using the molecular orbital nomenclature, the sigma (σ) portion of the metal-ligand bond would be formed by donnation of an unshared electron pair from the ligand, and the pi (π) portion by the back donnation of an electron pair from the filled d-levels of the metal. The formation of such a double bond would require that the electrons within the ligand rearrange themselves, giving rise to the observed frequency changes in the inorganic compounds. The donor atom of the ligand will be influenced by the properties of the cation. With increasing 'b'-type characteristics[102] having filled d levels, the probability of bonding through the sulphur increases. This may be attributed to the vacant 3d-levels on the sulphur which can accept electrons from the t_{2g} level of the metal ion. When the metal is 'a'-type then the more electrovalent nitrogen will provide a stronger σ donor. This picture of the bonding in thiocyanates has been supported by the behaviour of platinum complexes. In $H_2Pt(SCN)_4$ the thiocyanate bonds through the sulphur atom but in cases in which strong acceptors are also part of the complex, eg.

trisubstituted phosphines, then the t_{2g} electrons of the central cation are less available for bonding to the sulphur and the metal-ligand bond forms through the nitrogen. Thus it would be expected that ions of the first transition series would bond through the nitrogen whilst those of the second and third series might be expected to bond through sulphur. This has been confirmed by crystal structure analysis.[105]

Jones[103] studied the spectra of potassium thiocyanate in aqueous solution and also in the solid state. He estimated the bond distances to be 1.17 Å and 1.61 Å for the carbon-nitrogen and the carbon-sulphur bonds, respectively. Using these distances and Pauling's formula[104], he estimated the relative amounts of the resonance forms to be,

$N \equiv C - S^-$ 71%.....(a).

$^-N = C = S$ 12%.....(b).

$^{2-}N - C \equiv S^+$ 17%.....(c).

Since structure (c) is less likely than structure (b) the distribution must be considered as approximate. These structures have been used to consider the possible forms of bonding[105].

Table (XXVII).

Free Ion.	MN Bond.	MS Bond.
(a) $N \equiv C - S^-$	(d) $M - \overset{+}{N} \equiv C - \bar{S}$	(g) $M - S - C \equiv N$
(b) $^-N = C = S$	(e) $\bar{M} = \overset{+}{N} = C = S$	(h) $M - \overset{+}{S} = C = \bar{N}$
(c) $^{2-}N - C \equiv S^+$	(f) $M - N = C = S$	(i) $\bar{M} = \overset{2+}{S} = C = \bar{N}$

X-ray analysis implies that; for SM bonds form (g) is important, for NM bonds form (f) and (d) occur. When the ligand co-ordinates through the nitrogen then a σ bond will be formed and the rearrangement within the liquid will favour a drift of electrons towards the donor atom. Structure (f) would be stabilised since it does not have an unfavourable electron distribution as in (e) (negative charge on metal ion). Similarly when the bonding occurs through the sulphur atom, structure (g) is stabilised since both (h) and (i) would not favour the electron drift to the donor atom. It can be seen that the metal sulphur bond should provide a non-linear MSCN grouping. For metal nitrogen bonds the grouping could be either linear or non-linear. The latter would be expected to produce two main CN frequences but this was not observed in the solution studies. Previous workers[106] decided that the CN frequency was not indicative of the donor atom because its frequency was affected by a number of factors. (Eg. other cations in the complex). The CS stretch appears to be more diagnostic of the ML bond and Turco and Pecile[108] assigned limits to the two possibilities. The MN range was taken as 780-860cm.$^{-1}$ and the MS as 690-720 cm^{-1}. From Table (XXVII) it can be seen that form (g) has more CS single bond characteristic than either (d) or (f) so that the frequency would be expected to be lower and similar to the organic thiols. The class 'b' metal ions, lead(II) and cadmium(II), would be most likely to bond through the sulphur.

From a Nujoll mull of the solids the following frequencies were obtained, ammonium thiocyanate was included as a reference compound.

Complex	CS stretch cm^{-1}
NH_4CNS	753
$Pb(CNS)_2$	755
$Cd(CNS)_2$	755

From these measurements there was no evidence that either lead(II) or cadmium(II) bonds through sulphur if Pecile's limits are accepted. X-ray analysis of $Pb(CNS)_2$ is being attempted in this department but the work is hindered by the similarity in atomic number of carbon and nitrogen. There is the possibility of a third type of bonding, involving the thiocyanate ion in which bridge structures of the type, SCN — M — SCN, are formed. It has been shown[109] that in these cases the CS frequency does not follow any qualitative limits but has an intermediate value. This almost certainly is the case for the cadmium and lead solids investigated. Nuclear magnetic resonance of N^{14} has been used to determine the nature of the bonding atom[110]. The MS complexes move the resonance downfield and the MN upfield from the free anion. It was significant that the cadmium complexes could not be classified by this method providing additional evidence for the possibility of bridge structures.

The effect which a ligand has on the orbital energy of a metal ion accounts for its position in the spectrochemical series. For any single metal ion it has been shown[111] that the relative position of the CNS group will be indicative of the bonding. If the bond forms through the nitrogen then the ligand's position will be approximately the same as chloride; if the bond is through the sulphur then it falls between water and ammonia, ie.,

$$Cl^- \sim {}^-SCN < F^- < H_2O < {}^-NCS < NH_3 < CN^-.$$

Recently fundamental vibrations, other than CS and CN stretch, have been studied and frequencies assigned to them[112]. These are MN or MS stretching and NCS bending vibrations. The latter has been used to identify the bonding atom. Nitrogen bonded compounds absorb about 470cm^{-1} while sulphur bonded compounds have a band around 420cm^{-1}. The hypothesis that MSC bonds are always non-linear have been supported by the multiplicity of the SCN bending vibrations.

Lewis[113] suggested that the preference of a metal to bond through the nitrogen or sulphur atom could be settled by the relative strength of the more covalent MS bond to the more ionic MN bond. Taking the covalent bond contribution as being proportional to the total ionisation potential of various metals in the same valency state, and the relative strengths of the ionic bonds as ne/r, where r is the metal ion's radius and ne its formal charge, then IP/$\frac{ne}{r}$ is related to the ratio of the strength of the bond, if covalent, to its strength, if ionic. For the divalent metals investigated this ratio is shown in Table (XXVIII).

Table (XXVIII).

Metal	IP e.v.	r Å	$IP/\frac{ne}{r} = R$
Mn^{2+}	23.03	0.80	9.2.
Co^{2+}	24.91	0.74	9.2
Ni^{2+}	25.78	0.72	9.3
Cu^{2+}	28.01	0.72	10.1
Zn^{2+}	27.35	0.74	9.8
Cd^{2+}	25.80	0.97	11.3
Pb^{2+}	22.40	1.2	13.4

The ratio gives a relative indication of the preference in bonding and it can be seen that the lead and cadmium complexes would favour bonding through sulphur.

Table (XXIX) contains the frequency of the CN stretch in the complexes and the frequency shift, $\Delta\nu$, from the free anion. A similar I.R. study of the monothiocyanate complexes of transition metals in aqueous solution has been reported by Fronaeus and Larsson[114].

Table (XXIX).

Complex	CN stretch cm^{-1}	$\Delta\nu cm^{-1}$
CNS^-	2,068 (2,066)	
$MnCNS^+$	2,090 (2,093)	22(27)
$CoCNS^+$	2,114 (2,112)	46(46)
$NiCNS^+$	2,122 (2,119)	54(53)
$CuCNS^+$	2,120 -	52 -
$ZnCNS^+$	2,110 (2,109)	42(43)
$CdCNS^+$	2,100	38
$PbCNS^+$	2,114	46

The data in parenthesis are from reference (114). Fronaeus found that there was a linear relationship between the log of the association constant for the reaction,

$$M^{2+} + CNS^{-} \rightleftharpoons MCNS^{+}$$

and the frequency shift $\Delta\nu$. This relationship is based on the assumption that $\Delta\nu$ is proportional to the enthalpy of co-ordination and further, that the entropy term is almost constant for a sequence of similar metal ions. Since in Table (XXIX) both values of $\Delta\nu$ for any one metal are comparable, it is interesting to extrapolate a value for the association constant for the copper complex using a value of $\Delta\nu = 50cm^{-1}$. If a linear relationship is to be maintained then the value of K for the copper complex would be less than that for the nickel complex, contrary to the Irving-William's order[115]. If the $\Delta\nu$ values are proportional to the enthalpy of co-ordination then their variation would be more likely to be related to the second Ionisation Potential since the calorimetric measurements conclusively show that, although the entropy change is almost constant for manganese(II), cobalt (II) and nickel(II), the value found for zinc monothiocyanate is much larger.

PART V

Heats of Ionization of EGTA.

Heats of Ionisation of EGTA.

In order to analyse calorimetrically data for the heat of formation of complexes of EGTA, di-(2-aminoethoxy)-ethanetetraacetic acid, with divalent metal ions, it was necessary to know with some certainty the equilibrium constants for the protonation of the anion,

$$H_2L^{2-} \rightleftharpoons HL^{3-} + H^+ ,$$

$$HL^{3-} \rightleftharpoons L^{4-} + H^+ .$$

In the present work values of k_3' and k_4' were measured at 5, 15, 25, and 35°C and values of the enthalpy changes ΔH_3 and ΔH_4 were obtained from the van't Hoff equation. It has been shown that this temperature coefficient method can give reliable values for the heat changes providing a sufficiently large temperature range is chosen for study[116]. The experiments were carried out at an ionic strength of 0.1M in order to conform with the calorimetric studies.

EXPERIMENTAL.

The percentage purity of each batch of EGTA was estimated in an ammonia buffer solution by titrating with a standard solution of calcium, the end point being indicated by eriochrome black[28]. Standard solutions of the di-potassium salt were prepared by adding sufficient carbonate-free potassium hydroxide to neutralise the first two ionizable hydrogens of the acid. These stock solutions were diluted to approximately 2×10^{-3}M and potassium chloride added to maintain the ionic strength at $0.1 mole.l^{-1}$. All distilled water used in making solutions was boiled and purged with carbon dioxide-free nitrogen. The potassium hydroxide solutions were prepared as in Part I.

Measurements of pH at constant ionic strength were made using a glass electrode in the following cell,

$$Ag\,|\,AgCl,\ HCl\,|\,glass\,|\,solution\,|\,0.1\ KCl\,|\,calomel.$$

The glass electrode was of the wide range variety, (E.I.L.type GH 35). The salt bridge contained a potassium chloride solution of the same ionic strength as th experimental solution to avoid leakage errors. Measurements of e.m.f.s were made with a Tye potentiometer using a Vibron Electrometer (E.I.L.Model 33B) as a null detector.

The electrode system was standardised using buffer solutions whose pHs were higher than the second equivalence point of EGTA. The values of pH of these buffer solutions at the temperatures investigated were taken from Bates[117].

Buffer	5°C	15°C	25°C	35°C
Borax	9.395	9.276	9.180	9.102
Phosphate 1:1	6.951	6.900	6.855	6.844
Phosphate 1:3:5	7.500	7.448	7.413	7.389

Flasks containing solutions were kept in a water thermostat (Part I). Additions of alkali were made from an Agla micrometer syringe through an extended glass tip drawn out to a fine capillary which was kept under the solution surface during the titration. The micrometer scale could be read to 0.0002ml. Titrations were carried out in a closed vessel in an atmosphere of nitrogen.

Results and Discussion.

The third and fourth dissociation constants of EGTA can be written,

$$k_3' = \frac{[H^+][HY^{3-}]}{[H_2Y_2^{2-}]} \quad , \quad k_4' = \frac{[H^+][Y^{4-}]}{[HY^{3-}]} \quad ,$$

and the electroneutrality is,

$$[H^+] + [K^+] = 2[H_2Y^{2-}] + 3[HY^{3-}] + 4[Y^{4-}] + [OH^-] .$$

If the total concentrations of the ligand and potassium hydroxide are termed C and B respectively, then an expression of the form,

$$y = -k_3'x - k_3'k_4' ,$$

can be obtained.

$$\frac{(B-2C-[OH^-])}{(B-4C-[OH^-])}[H^+]^2 = -k_3' \frac{(B-3C-[OH^-])}{(B-4C-[OH^-])}[H^+] - k_3'k_4' . \quad \ldots\ldots\ldots(34).$$

Plots of y versus x were made at each temperature and are shown in Fig(7) . For each temperature fifteen points were calculated (Table XXX), lying between pH 8 and 10, this being considered the upper limit of the glass electrode.

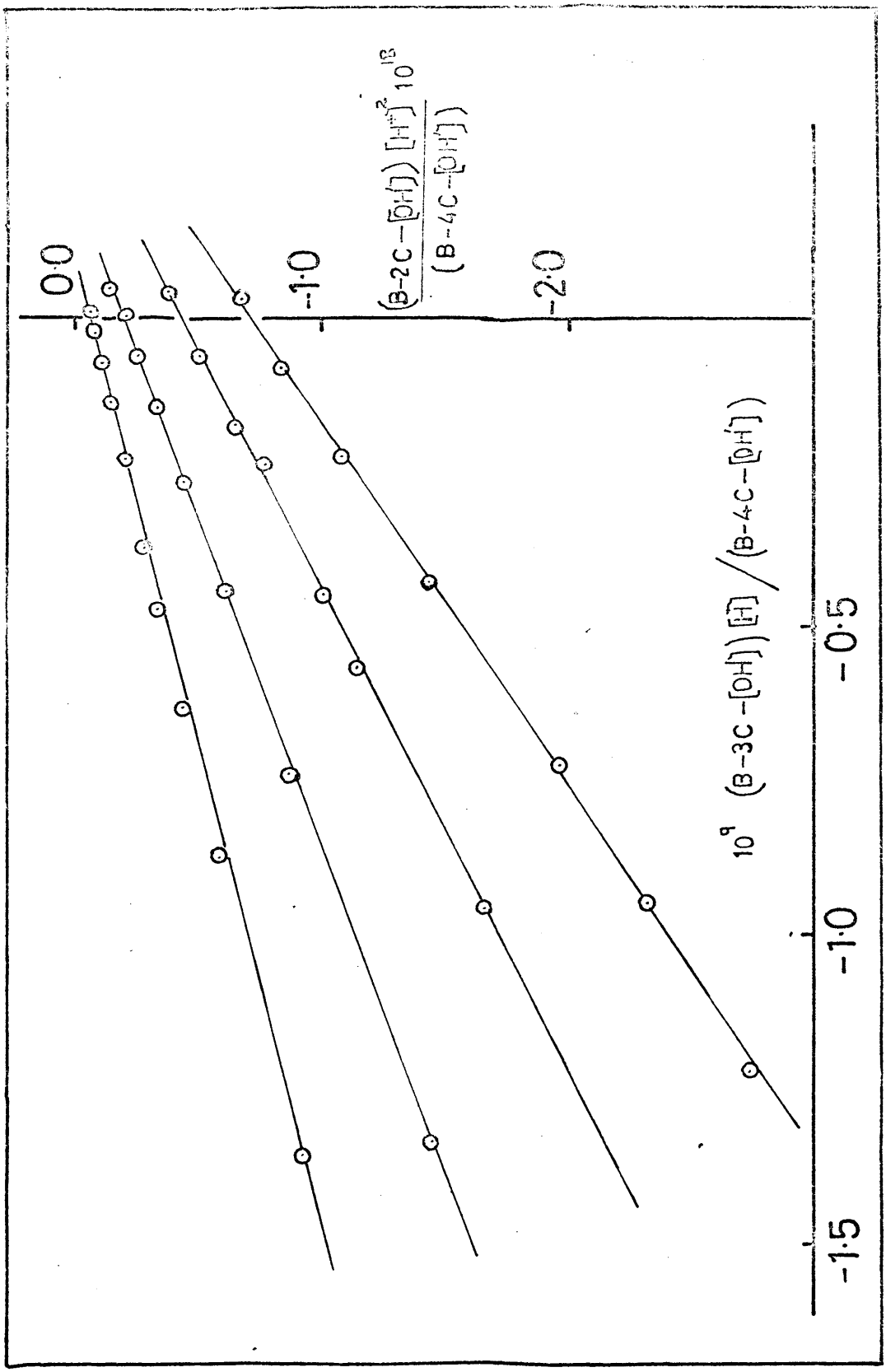


Fig. 7.

Values of the ionic product of water for the temperatures investigated were taken from Harned and Owen[118].

The values of k_3' and k_4' over the temperature range investigated are shown in Table (XXXI) and graphs of $\log k_3'$ and $\log k_4'$ versus 1/T are shown in Fig(8).

Table (XXX).

molar concentrations at 5°C.

pt.	C x 10^3	B x 10^3	pH	-y x 10^{19}	χ' x 10^9
1	1.957	4.130	8.28	16.020	-2.472
2	1.956	4.278	8.52	9.560	-1.355
3	1.956	4.402	8.69	5.929	-0.875
4	1.956	4.527	8.81	4.445	-0.631
5	1.956	4.651	8.91	3.489	-0.472
6	1.955	4.773	8.99	2.933	-0.368
7	1.955	5.021	9.14	2.069	-0.220
8	1.954	5.268	9.27	1.522	-0.127
9	1.953	5.515	9.38	1.203	-0.064
10	1.953	5.763	9.49	0.932	-0.018
11	1.952	6.009	9.60	0.722	.018
12	1.952	6.504	9.82	0.438	0.059
13	1.951	6.992	10.07	0.252	0.105
14	1.951	7.492	10.41	0.088	0.945
15	1.951	7.984	10.91	0.017	0.718

Table (XXX) Contd.

molar concentrations at 15°C.

Pt.	C x 10^3	B x 10^3	pH	-y x 10^{19}	χ' x 10^9
1	1.953	4.155	8.15	34.0	-3.302
2	1.952	4.404	8.50	14.6	-1.342
3	1.952	4.641	8.71	8.97	-0.745
4	1.951	4.901	8.87	6.21	-0.445
5	1.951	5.149	9.01	4.43	-0.252
6	1.950	5.398	9.13	3.37	-0.143
7	1.950	5.646	9.24	2.63	-0.058
8	1.949	5.893	9.35	2.07	0.006
9	1.949	6.145	9.46	1,59	0.054
10	1.948	6.390	9.57	1.24	0.091
11	1.947	6.760	9.74	0.86	0.145
12	1.947	7.131	9.94	0.56	0.186
13	1.946	7.347	10.05	0.41	0.198
14	1.945	7.507	10.19	0.34	0.227
15	1.945	7.712	10.36	0.23	0.242

Table (XXX) Contd.

molar concentrations at 25°C.

Pt.	C x 10^3	B x 10^3	pH	-y x 10^{19}	χ' x 10^9
1	1.953	4.328	8.30	36.10	-2.421
2	1.953	4.453	8.38	28.32	-1.740
3	1.952	4.703	8.59	16.72	-0.963
4	1.952	4.951	8.75	11.83	-0.572
5	1.952	5.076	8.81	10.19	-0.451
6	1.951	5.348	8.94	7.71	-0.240
7	1.951	5.449	9.00	6.44	-0.179
8	1.951	5.694	9.11	5.10	-0.058
9	1.950	5.953	9.21	4.11	0.039
10	1.949	6.196	9.31	3.32	0.090
11	1.949	6.438	9.43	2.56	0.149
12	1.948	6.694	9.53	1.24	0.191
13	1.947	7.191	9.78	1.29	0.310
14	1.946	7.566	10.00	1.02	0.460

Table (XXX) Contd.

molar concentrations at 35°C.

Pt.	C x 10^3	B x 10^3	pH	-y x 10^{19}	χ' x 10^9
1	1.947	4.326	8.17	56.73	-2.960
2	1.947	4.447	8.29	33.10	-2.143
3	1.947	4.571	8.40	33.10	-1.574
4	1.946	4.693	8.48	27.49	-1.215
5	1.946	4.817	8.56	23.38	-0.950
6	1.945	4.941	8.64	19.17	-0.725
7	1.945	5.187	8.77	14.31	-0.429
8	1.944	5.432	8.89	10.82	-0.225
9	1.944	5.680	9.00	8.41	-0.079
10	1.944	5.927	9.10	6.81	0.032
11	1.943	6.048	9.21	4.63	0.068
12	1.943	6.172	9.32	3.16	0.091
13	1.943	6.419	9.49	1.86	0.125
14	1.942	6.911	9.75	0.98	0.187
15	1.942	7.404	10.06	0.46	0.223

Table (XXXI).

Dissociation Constants of EGTA.

T°C	5	15	25	35
k_3' x 10^{10}	6.25	9.70	13.3	16.9
k_4' x 10^{10}	1.13	2.06	2.93	4.14

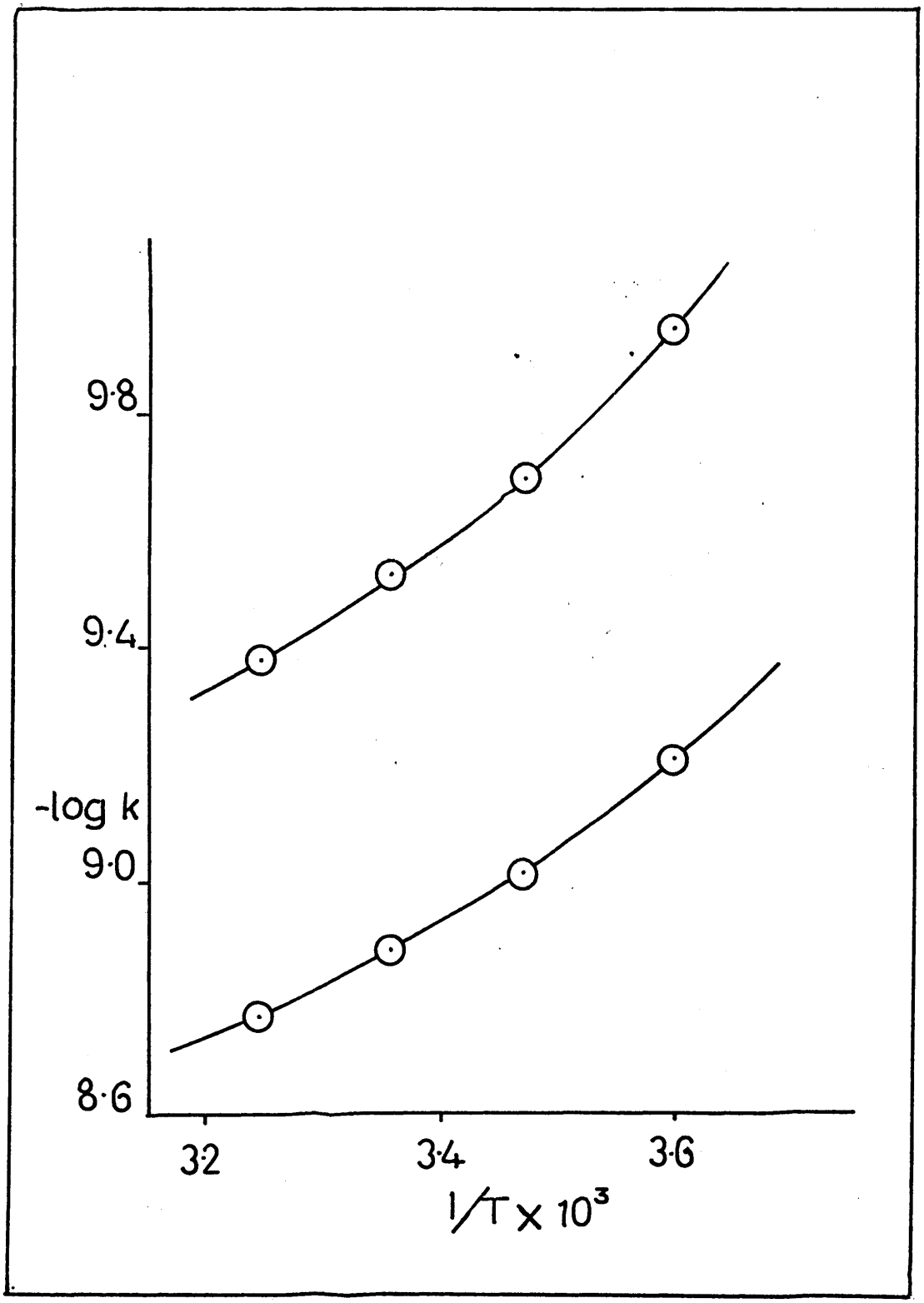


Fig. 8

The interpolated values at 20°C, $k_3' = 11.32 \times 10^{-10}$, and $k_4' = 2.54 \times 10^{-10}$ are in good agreement with the values 11.28×10^{-10} and 2.78×10^{-10} respectively, calculated from the concentration constants of Schwarzenbach, Senn and Anderegg[119], by introducing a value for the activity coefficients of the hydrogen ion $f_{H^+} = f_{\pm}(HCl) = 0.799$ in 0.1M hydrochloric acid[118].

The variation of k_3' and k_4' with temperature may be expressed with an accuracy of better than 1% in k_3' and k_4', by the equation,

$$\log k = a + bT + cT^2$$

hence, $$\Delta H = 2.3RT^2(b+2cT)$$

and the derived thermodynamic functions for the dissociation reactions are, $\Delta H_3 = 4.88$, $\Delta H_4 = 6.33$ k.cal.mole^{-1}, $\Delta S_3 = -24.2$ and $\Delta S_4 = -22.4$cal.deg.$^{-1}$mole^{-1} at 25°C. The values of ΔH at 20°C to be compared with Anderegg's calorimetric values[120] of $\Delta H_3 = 5.76$ and $\Delta H_4 = 5.84$k.cal.mole^{-1} are 5.4 and 6.1 k.cal.mole^{-1} respectively. The agreement is good and in addition the present temperature coefficient data may be used to calculate an approximate value for the change in heat capacity for these dissociation reactions from the equation,

$$\Delta C_p = 4.606RT\,(b+3cT).$$

The value, -48 ± 20cal.deg.$^{-1}$mole^{-1} (for ΔC_{p3}) is similar

to that obtained for other weak acid dissociation reactions[121].

Appendix.

In addition to the work described in Parts I - V ofthis thesis, a number of systems have been studied which do not fit into the pattern of study. The results and essential details are given below.

Heat of Formation of Copper Succinate at $I = 0.2 mole.l^{-1}$

$k_1' - 1.38 \times 10^{-4}$ $k_2' - 6.90 \times 10^{-6}$ $K = 1.81 \times 10^3$

molar concentrations (Ref 45)

$m_1 \times 10^3$	$m_2 \times 10^3$	CuSucc $\times 10^3$	ΔH_I
3.023	10.699	2.825	1.56
2.882	10.197	2.686	1.63
2.796	6.028	2.424	1.70

Mean $\Delta H = 1.63 \pm 0.05$ k.cal.mole^{-1}.

Heat of Formation of Nickel Monothiocyanate at

$I = 0.5 molel^{-1}$

$K = 15$

$m_1 \times 10^3$	$m_2 \times 10^3$	$NiCNS^+ \times 10^4$	ΔH_I
4.121	6.721	3.192	-3.49
4.386	4.503	4.193	-3.54

Mean $\Delta H = -3.51 \pm 0.03$k.cal.mole^{-1}.

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